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Organic Chemistry.

Silver-sulphochromic Oxidation of Coal. L. J. Simon (*Compt. rend.*, 1924, **178**, 775—777).—When coal is heated with a mixture of silver dichromate and concentrated sulphuric acid at 100°, 4—5% of the carbon present remains unoxidised. Formation of gaseous oxidation products is more rapid at 50° than at 60°, at which temperature 28% of the coal remains unchanged, about 6·7% being rendered soluble. When powdered coke is oxidised by chromic acid, 54·2% is unaffected, as against 39% when silver dichromate is used. It is concluded from the results that coal contains two constituents intimately mixed. One is oxidised at low temperatures, the other, like coke, requiring a temperature of 100°. E. E. T.

Composition of Natural Gas Gasoline. R. P. Anderson and A. M. Erskine (*J. Ind. Eng. Chem.*, 1924, **16**, 263—267).—Fractional distillation shows that the approximate composition of this gasoline is: propane and butanes, 20% (by volume); *iso*-pentane, 13%; *n*-pentane, 17%; *iso*hexane, 9%; *n*-hexane, 15%; *iso*heptane, 8%; *n*-heptane, 12%; octane, 4%, and absorption oil, 2%; the presence of traces of benzene and toluene is indicated. C. I.

Composition of Low-temperature Tar. IV. F. Schütz, W. Buschmann, and H. Wissenbach (*Ber.*, 1924, **57**, [*B*], 421—423; cf. A., 1923, i, 1080).—An examination of the requisite C_9 to C_{12} fraction of neutral oil from low-temperature coal-tar showed that 80—86% consists of unsaturated and aromatic hydrocarbons, whilst the remaining 14—20%, boiling from 30° to 220°, probably contains *n*-nonane, *n*-decane, *n*-undecane, and *n*-dodecane, as indicated by the boiling points of the fractions, although the densities are slightly too high. [Cf. *B.*, 1924, 367.] F. A. M.

Action of Sodamide on True Acetylene Hydrocarbons. Bourguel (*Compt. rend.*, 1924, **178**, 777—779; cf. A., 1923, i, 1176).—When chloro-compounds are treated, by the author's method, with sodamide, the acetylene hydrocarbon is never present as such at the end of the reaction, but as a sodamide or sodium derivative of the hydrocarbon. If pure pentinene, diluted with xylene, is added to a xylene suspension of sodamide heated at 120°, 1 mol. of ammonia is evolved per mol. of pentinene, with formation of a sodium derivative of the latter. E. E. T.

Chlorination of Butylene and the Properties of Dichlorobutane. E. Briner, J. Hausser, and E. de Luserna (*Helv. Chim. Acta*, 1924, **7**, 374—376).—*n*-Butyl alcohol is readily

converted into butylene by passage over alumina at 480°. Butylene combines with chlorine, with evolution of heat, forming dichlorobutane, the molecular heat of reaction being 33·4 Cal. The reaction is not explosive. Dichlorobutane has b. p. 114·6—114·8°/730 mm.; n^{20} 1·4325; d^{0} 1·144, $d^{22·2}$ 1·115, $d^{99·5}$ 1·032; ignition temperature, 62°. The viscosity coefficient is 0·0515 at 0°, 0·01073 at 22·2°, 0·00535 at 99·5°. It is a good solvent for oils and fats and is not poisonous. E. H. R.

Action of Ammonia on Organic Halogen Compounds at High Temperature. J. Heslinga (*Rec. trav. chim.*, 1924, **43**, 178—180).—The halogen in organic compounds containing chlorine or bromine is quantitatively converted into ammonium halide when the substance is heated to redness in a current of ammonia. Chloro derivatives of benzene, if substituted in the ring, are exceptions to the general rule. (Cf. this vol., ii, 55.) H. J. E.

Near Ultra-red Absorption Spectra of some Organic Liquids. J. W. Ellis.—(See this vol., ii, 218.)

Analogues of Citronellol Richer and Poorer in Carbon. I. J. von Braun and R. Gossel (*Ber.*, 1924, **57**, [*B*], 373—382).—The effect of the position of the double bond and of the number and position of the methyl groups on the odour of citronellol, $CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, has been examined. The conversion of the terminal group, $CMe_2{:}C-$, into the complex, $CH_2{:}C-$, causes a very marked alteration in odour which is less marked when the group is $CHMe{:}C-$; the introduction of further methyl radicals (in addition to the γ-methyl group) does not cause an appreciable change in odour, whence it is probable that the γ-methyl group is itself unimportant. The decisive factor appears to be the presence of the group $CMe_2{:}C-$, or to a less extent of $CHMe{:}C-$, at a definite distance from the primary alcoholic group. The alcohols described in the present communication are optically inactive, but the comparison of them with optically active citronellol is regarded as justifiable, since, in general, little difference in odour is observed between isomeric active and racemic substances.

Δ^{δ}-Butenyl bromide reacts readily with an alcoholic solution of ethyl sodioacetoacetate to give a mixture of *ethyl butenylacetoacetate*, $CH_3{\cdot}CO{\cdot}CH(CH_2{\cdot}CH{:}CHMe){\cdot}CO_2Et$, a mobile liquid, b. p. 112—114°/11 mm., and *ethyl dibutenylacetoacetate*, b. p. 135—137°/12 mm. The former ester is hydrolysed by dilute, aqueous potassium hydroxide solution to *Δ^{δ}-heptene-ζ-one*, $CHMe{:}CH{\cdot}[CH_2]_2{\cdot}COMe$, b. p. 152—155°/atmospheric pressure, 42—43°/9 mm., d_4^{20} 0·8446, n_D^{20} 1·4292 (*semicarbazone*, lustrous leaflets, m. p. 97°). *Ethyl methylbutenylacetoacetate*, $CH_3{\cdot}CO{\cdot}CMe(CH_2{\cdot}CH{:}CHMe){\cdot}CO_2Et$, b. p. 120—122°/20 mm., is hydrolysed to *γ-methyl-Δ^{ϵ}-heptene-β-one*, $CHMe{:}CH{\cdot}CH_2{\cdot}CHMe{\cdot}COMe$, b. p. 62—64°/20 mm., d_4^{18} 0·8463, n_D^{18} 1·4345, which resembles amyl acetate in odour.

Ethyl β-methyl-$\Delta^{\alpha\epsilon}$-heptadienoate, a colourless liquid, b. p. 103—105°/22 mm., prepared by the action of potassium hydrogen

sulphate at 150° on ethyl β-hydroxy-β-methyl-$\Delta^{\alpha\epsilon}$-heptadienoate, is reduced by sodium and alcohol to *γ-methyl-Δ$^{\zeta}$-heptenol*,

$$CH_2{:}CH{\cdot}[CH_2]_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH,$$

b. p. 97—99°/22 mm., d_4^{19} 0·8562, n_D^{19} 1·4470, which has no resemblance in odour to citronellol.

Δ^{β}-Hexene-ζ-one is transformed by zinc and ethyl α-bromopropionate into *ethyl β-hydroxy-αβ-dimethyl-Δ$^{\epsilon}$-heptenoate*,

$$CH_2{:}CH{\cdot}[CH_2]_2{\cdot}CMe(OH){\cdot}CHMe{\cdot}CO_2Et,$$

a somewhat viscous, colourless, odourless liquid, b. p. 124—126°/18 mm., which is hydrolysed to the corresponding *acid*, a colourless, viscous liquid with a very unpleasant odour, b. p. 175—176°/18 mm. The latter compound is converted by acetic anhydride and anhydrous sodium acetate into *αβ-dimethyl-$\Delta^{\alpha\epsilon}$-heptadienoic acid*,

$$CH_2{:}CH{\cdot}[CH_2]_2{\cdot}CMe{:}CMe{\cdot}CO_2H,$$

an unpleasant smelling liquid, b. p. 145—146°/18 mm., from which *ethyl αβ-dimethyl-$\Delta^{\alpha\epsilon}$-heptadienoate*, b. p. 103—105°/18 mm., is prepared. The ester is reduced by sodium and alcohol to *βγ-dimethyl-Δ$^{\zeta}$-heptenol*, $CH_2{:}CH{\cdot}[CH_2]_2{\cdot}CHMe{\cdot}CHMe{\cdot}CH_2{\cdot}OH$, b. p. 101—102°/20 mm., d_4^{21} 0·8741, n_D^{21} 1·4570, the odour of which is quite distinct from that of citronellol.

Ethyl β-hydroxy-αβγ-trimethyl-Δ$^{\epsilon}$-heptenoate,

$$CH_2{:}CH{\cdot}CH_2{\cdot}CHMe{\cdot}CMe(OH){\cdot}CHMe{\cdot}CO_2Et,$$

a viscous liquid with a very faint odour, b. p. 123—125°/17 mm., is readily obtained from γ-methyl-Δ$^{\epsilon}$-heptene-β-one, zinc, and ethyl α-bromopropionate. Complete dehydration of this compound or of the corresponding hydroxy acid could not be accomplished. The incompletely homogeneous βγδ-trimethyl-Δ$^{\zeta}$-heptenol,

$$CH_2{:}CH{\cdot}CH_2{\cdot}[CHMe]_3{\cdot}CH_2{\cdot}OH,$$

does not, however, resemble citronellol in odour.

Ethyl β-hydroxy-β-methyl-Δ$^{\epsilon}$-octenate,

$$CHMe{:}CH{\cdot}[CH_2]_2{\cdot}CMe(OH){\cdot}CH_2{\cdot}CO_2Et,$$

b. p. 121—122°/10 mm., is hydrolysed to the corresponding *acid*, a viscous liquid, b. p. 177—180°/16 mm., which is transformed by sodium acetate and acetic anhydride into *β-methyl-$\Delta^{\alpha\epsilon}$-octadienoic acid*, $CHMe{:}CH{\cdot}[CH_2]_2{\cdot}CMe{:}CH{\cdot}CO_2H$, b. p. 149—150°/18 mm., from which *ethyl β-methyl-$\Delta^{\alpha\epsilon}$-octadienoate*, b. p. 114—115°/18 mm., is obtained. The ester is readily reduced by sodium and alcohol to *γ-methyl-Δ$^{\zeta}$-octenol* (*norcitronellol*),

$$CHMe{:}CH{\cdot}[CH_2]_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH,$$

b. p. 109—111°/20 mm., d_4^{20} 0·8674, n_D^{20} 1·4560, which has a terpene-like odour with a faint resemblance to that of citronellol. *β-Methyl-Δ$^{\epsilon}$-octenoic acid*, $CHMe{:}CH{\cdot}[CH_2]{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$, b. p. 145—146°/18 mm., is obtained as by-product of the reduction; the corresponding *ethyl* ester has b. p. 109—111°/21 mm.

Ethyl β-hydroxy-αβ-dimethyl-Δ$^{\epsilon}$-octenoate,

$$CHMe{:}CH{\cdot}[CH_2]_2{\cdot}CMe(OH){\cdot}CHMe{\cdot}CO_2Et,$$

b. p. 139—142°/20 mm., is converted by potassium hydrogen sulphate into *ethyl αβ-dimethyl-$\Delta^{\alpha\epsilon}$-octadienoate*,

$$CHMe{:}CH{\cdot}[CH_2]_2{\cdot}CMe{:}CMe{\cdot}CO_2Et,$$

a liquid with a tolerably pleasant odour, b. p. 115—116°/19 mm., and the corresponding *acid*, an unpleasant smelling liquid, b. p.

152—155°/20 mm. The ester is reduced by sodium and alcohol to *βγ-dimethyl-Δ$^{\zeta}$-octenol*, $CHMe{:}CH{\cdot}[CH_2]_2{\cdot}[CHMe]_2{\cdot}CH_2{\cdot}OH$, b. p. 111—112°/21 mm., d_4^{21} 0·8775, n_D^{21} 1·4670, which resembles the terpenes and citronellol in odour.

Ethyl β-hydroxy-βγ-dimethyl-Δ$^{\epsilon}$-octenoate,

$$CHMe{:}CH{\cdot}CH_2{\cdot}CHMe{\cdot}CMe(OH){\cdot}CH_2{\cdot}CO_2Et,$$

an odourless liquid, b. p. 137—139°/20 mm., is transformed successively into *ethyl βγ-dimethyl-Δ$^{\alpha\epsilon}$-octadienoate*, a very pleasant smelling liquid, b. p. 123—124°/20 mm., and *γδ-dimethyl-Δ$^{\zeta}$-octenol*, $CHMe{:}CH{\cdot}CH_2{\cdot}[CHMe]_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, b. p. 114—115°/17 mm., d_4^{19} 0·8775, n_D^{19} 1·465, which is allied to citronellol in odour.

Methylheptenone, zinc, and ethyl α-bromopropionate yield *ethyl β-hydroxy-αβζ-trimethyl-Δ$^{\epsilon}$-octenoate*,

$$CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}CMe(OH){\cdot}CHMe{\cdot}CO_2Et,$$

a colourless, viscous liquid, b. p. 145°/16 mm., which is transformed by potassium hydrogen sulphate at 150° into *ethyl αβζ-trimethyl-Δ$^{\alpha\epsilon}$-octadienoate*, b. p. 126—128°/20 mm. The latter ester is smoothly reduced to *βγη-trimethyl-Δ$^{\zeta}$-octenol* (*homocitronellol*),

$$CMe_2{:}CH{\cdot}[CH_2]{\cdot}[CHMe]_2{\cdot}CH_2{\cdot}OH,$$

a mobile liquid, b. p. 125—127°/20 mm., d_4^{17} 0·8860, n_D^{17} 1·4725. The odour of the substance is more closely similar to that of citronellol than are those of the alcohols containing the terminal group, $CHMe{:}C^-$. When preserved, it exhibits the same change and refinement of odour which is characteristic of citronellol, and is possibly due to an establishment of an equilibrium between two forms containing the groups, $CMe_2{:}C^-$ and $CH_2{:}CMe{\cdot}C^-$. H. W.

Manufacture of Ether. J. Desmaroux (*Mém. Poudres*, 1923, **20**, 335—390).—The system, H_2SO_4–EtOH–H_2O–Et_2O–$EtHSO_4$, is considered theoretically, and a diagram is evolved showing the interdependence of the concentrations of the various components. Phase-rule considerations show that the system has three degrees of freedom. The state of equilibrium, particularly with regard to ether, is practically independent both of the temperature and of the sulphuric acid concentration. The experimental results obtained are in excellent agreement with the formulæ $Y=m(1-10^{-ht})$ and $X=r(1-S.10^{kt})$ where Y=the percentage of alcohol converted into ether and X=the percentage of free acid in the mixture at the end of time t. Tables giving the values of the constants m, h, r, k, and S for the various temperatures and concentrations of sulphuric acid and alcohol are appended. A comprehensive thermodynamic study of the conditions of the reaction enables results to be deduced which are in general agreement with practical experience of ether manufacture. A laboratory investigation of the nature of the vapour given off showed that with a fall in the acidity of the mixture the quantity of alcohol in equilibrium with it increases and the proportion of ether in the vapour falls. [Cf. *B.*, 1924, 313.] H. C. R.

Termolecular Gas Reactions. I. Mechanism of the Formation of Acetic Acid from Acetaldehyde and Oxygen. A. Kiss and L. Demény (*Rec. trav. chim.*, 1924, **43**, 221—248).—The reaction between pure acetaldehyde and pure oxygen was examined

by the method previously described (A., 1923, ii, 237), the theory developed by Trautz (A., 1918, ii, 151) being applied. If the formation of an intermediate compound, $CH_3{\cdot}CHO,O_2$, is postulated: $CH_3{\cdot}CHO + O_2 = CH_3{\cdot}CHO,O_2$; $CH_3{\cdot}CHO,O_2 + CH_3{\cdot}CHO = 2CH_3{\cdot}CO_2H$, the velocity constant passes through a maximum with lapse of time, which suggests catalytic action. The reaction was also studied in presence of water vapour. At 20°, a long period of induction (10 hours) set in; at 60—80°, the induction period was shorter than for the dry gases at the same temperatures. These results showed that the action was autocatalytic, the formation of the autocatalyst being accelerated by moisture. The experimental results did not indicate whether the catalysis was chemical or physical. The autocatalyst is probably acetic acid: $CH_3{\cdot}CHO+CH_3{\cdot}CO_2H \rightleftharpoons CH_3{\cdot}CHO,CH_3{\cdot}CO_2H$ (infinitely rapid); $CH_3{\cdot}CHO,CH_3{\cdot}CO_2H+O_2 = CH_3{\cdot}CO_2H+CH_3{\cdot}CHO,O_2$ (measurable speed). The formation of this intermediate compound was shown to be a true gas reaction of the second order, catalysed by acetic acid but uninfluenced by water. With increasing oxygen pressure, the reaction is retarded; excess of aldehyde accelerates it, which seems to point to the complex $CH_3{\cdot}CHO,CH_3{\cdot}CO_2H$ as the catalyst. Indifferent gases (nitrogen, carbon dioxide) exerted no influence, neither, apparently, did the surface of the containing vessel. The reaction was not sensitive to light. S. K. T.

Ammonium Oleate. M. Mlodziejevski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 471—478).—Ammonium oleate when gently heated with alcohol dissolves, and on cooling crystallises in the form of plates possessing double refraction. When it is heated more strongly and then allowed to cool, a fine emulsion possessing double refraction is formed. This is followed by the appearance of fluid crystals in the form of "puppets" and sometimes also liquid spherolites and oily strips. On further cooling, the liquid crystals disappear; an emulsion is temporarily formed which is then followed by the appearance of the solid crystals. The same changes can be studied repeatedly on a single microscopic slide. S. P. S.

Simple and Mixed Acid Anhydrides. W. Autenrieth and G. Thomae (*Ber.*, 1924, **57**, [*B*], 423—437; cf. A., 1901, i, 185).—It is shown that it is not possible to prepare mixed aliphatic–aromatic or aromatic–aromatic anhydrides either by the action of acetic anhydride on aromatic acids or by the action of the acid chloride on the sodium salt of another acid. The reaction given in Beilstein's "Handbuch" (3 *Aufl.*, **1**, 461): $(C_2H_3O)_2O+2C_2H_5{\cdot}OH = 2C_2H_3O_2{\cdot}C_2H_5+H_2O$, is shown to be incorrect, as in all cases examined 1 mol. of anhydride yielded only 1 mol. of ester and 1 mol. of free acid.

Ammonia, phenylhydrazine, and aniline react with aromatic anhydrides to give 1 mol. of free acid and 1 mol. of the acid amide, anilide, or hydrazide. Hydrazine hydrate reacts with *p*-toluic anhydride to give *s*-di-*p*-toluoylhydrazine, whilst a 50% aqueous solution of the base yields the monoacyl derivative,

$$C_6H_4Me{\cdot}CO{\cdot}NH{\cdot}NH_2.$$

p-Bromobenzoic anhydride yields only p-*bromobenzoylhydrazine*, m. p. 167°. The following anhydrides were prepared by the action of acetic anhydride on the requisite acid: stearic anhydride, m. p. 70—71°; palmitic anhydride, m. p. 62—63°; phenylacetic anhydride, prisms, m. p. 71—72°; *o*-toluic anhydride, m. p. 38—39°; m-*toluic anhydride*, prisms, m. p. 70—71°; *p*-toluic anhydride, leaflets, m. p. 95°; *p*-bromobenzoic anhydride, white plates, m. p. 218°; m-*nitrobenzoic anhydride*, prisms, m. p. 159—160°; p-*ethoxybenzoic anhydride*, m. p. 108° (which yields with aniline p-*ethoxybenzanilide*, m. p. 169°). The following new compounds are also noted: *Phenyl phenylacetate* (from phenylacetic anhydride and phenol), prisms, m. p. 42°. p-*Tolyl phenylacetate*, prisms, m. p. 75—76°. p-*Tolyl* p-*toluate* (from *p*-toluic anhydride and *p*-cresol), plates, m. p. 91—92°. F. A. M.

The Influence of Constitution on the Catalytic Hydrolysis of Esters by Acids. G. Berger (*Rec. trav. chim.*, 1924, **43**, 163—177).—The rate of hydrolysis of about twenty esters of monobasic fatty acids and of substituted acetic and benzoic acids was studied. The catalyst used was *N*/10-hydrochloric acid and the medium of hydrolysis a mixture of alcohol and water containing 42·34% of alcohol. Experiments were carried out at different temperatures owing to the variation in ease of hydrolysis shown by the esters, and in calculating the reaction-velocity the presence of ethyl alcohol as solvent was recognised as a factor in the case of ethyl esters. The author draws the conclusions that the acceleration of hydrolysis brought about by hydrogen ions decreases with the strength of the ester acid (cf. Olivier and Berger, A., 1923, ii, 144) and, in the case of esters with negative alcoholic groups, *i.e.*, where the alcoholic constituent possesses a somewhat acid character, the acceleration is small. In the case of methyl and ethyl esters of the same acid, the difference in reaction velocity is not constant but decreases with the acidity of the ester. The accelerated action in the case of an ester of the type $R'\cdot CO_2R''$ is thus conditioned by both the R′ and R″ groups, and these groups appear to be of equal importance and strength in their influence on hydrolysis from both the qualitative and quantitative points of view. H. J. E.

Monocarboxylic Acids derived from Sugars. II. Methylation of Tetramethyl-gluconic Acid. J. Pryde (*J. Chem. Soc.*, 1924, **125**, 520—522).—Tetramethyl-gluconolactone, treated with one molecular proportion of water, and then with methyl iodide and silver oxide at 40°, yields *methyl tetramethyl-gluconate*, $OMe\cdot CH_2\cdot CH(OMe)\cdot CH(OH)\cdot [CH(OMe)]_2\cdot CO_2Me$, a neutral, mobile oil, n_D^{15} 1·4480. On subjecting this to five successive methylations, *methyl pentamethyl-gluconate* was obtained as a neutral, colourless, limpid, very mobile oil, b. p. 100°/1·0 mm., n_D^{15} 1·4412, $[\alpha]_{5461}$ +42·7° in alcohol, and +24·9° in water, falling to +21·9° in 4 months. F. G. W.

Oils in the Chaulmoogra Group. G. A. Perkins and A. O. Cruz (*Philippine J. Sci.*, 1923, **23**, 543—569).—The oils from the

seeds of the following species were examined : *Gynocardia odorata*, *Hydnocarpus alcalœ*, *H. anthelminthica*, *H. Hutchinsonii*, *H. subfalcata*, *H. venenata*, *H. Wightiana*, *H. Woodii*, *Pangium edule*, and *Taraktogenos Kurzii*. The data obtained show a close similarity between the true chaulmoogra oil (from *Taraktogenos Kurzii*) and all the *Hydnocarpus* oils investigated. The oil from *Hydnocarpus alcalœ* is distinguished by its very high content of chaulmoogric acid. It contains little or no hydnocarpic acid. The other *Hydnocarpus* oils, like chaulmoogra oil, may each be separated by the distillation of the ethyl esters into fractions, one of which contains the acids with 16 carbon atoms and the other those with 18 carbon atoms. The former fractions of each oil contain hydnocarpic acid and an unknown acid or acids which cannot be completely separated from the hydnocarpic acid by one recrystallisation from 80% alcohol. This unknown acid portion has a lower optical activity than hydnocarpic acid. The latter fractions (acids with 18 carbon atoms) contain chaulmoogric acid, which can be separated more readily than hydnocarpic acid. A more highly unsaturated portion is left in the case of many samples when the chaulmoogric acid is crystallised out. Previous results placing *Gynocardia odorata* outside the chaulmoogra group were confirmed. *Pangium edule* seeds appear to contain no chaulmoogric or hydnocarpic acids. H. C. R.

Compounds Developed in Rancid Fats, with Observations on the Mechanism of their Formation. W. C. Powick (*J. Agric. Res.*, 1923, **26**, 323—362).—A large number of possible products of rancidity in fats have been examined. It is suggested that nonaldehyde is in part responsible for the odour of rancid fats. The glyceryl radical and the unsaponifiable portion of fats appeared to have no part in the phenomena of rancidity, which may be reproduced by the oxidation of oleic acid. The colour developed in the Kreis test for rancidity was spectroscopically identical with that obtained by applying the test to a mixture of acraldehyde and hydrogen peroxide, and the essential compound appeared to be epihydrin aldehyde. Whilst this compound did not occur in rancid fats, a derivative, probably the acetal, is suggested as being the parent substance which is decomposed on the addition of hydrochloric acid in the Kreis test. A number of substances give a red coloration with phloroglucinol–hydrochloric acid, and spectroscopic examination is necessary to obtain positive evidence of rancidity. A possible mechanism for the formation of epihydrin aldehyde or its parent substance from fats is described. A. G. P.

Reactivity of Iodine towards Fats. III. Production of Acidity in the Reaction and the Mechanism of its Formation. B. M. Margosches and W. Hinner (*Chem. Umschau*, 1924, **31**, 41—45).—Acids are produced in the reaction between fats or unsaturated fatty acids and iodine solutions, the quantity varying with the solvent used for the iodine. Brown iodine solutions obtained with aqueous solvents or solvents miscible with water, from which an amount of iodine is absorbed by the fat which

almost corresponds with its iodine value (Hübl), give a large amount of acid, corresponding with about half the iodine absorbed. Solutions of iodine in carbon tetrachloride, however, produce no acid in their action on fats, and other violet iodine solutions (in benzene, chlorinated ethylenes, and chloroform) give varying but comparatively small amounts of acid when they react on fats. In the action of aqueous and alcoholic iodine solutions on fats, an additive product of hypoiodous acid and the unsaturated molecule is formed, and not a simple iodine additive product as commonly supposed. This view is supported by the qualitative and quantitative production of acid. The action is analogous to Wijs' explanation of the action of his iodine monochloride solution on unsaturated linkings. The iodine from violet iodine solutions is mainly absorbed by unsaturated fats as such, but the reaction does not by any means proceed to completion. In the case of brown iodine solutions, the active mass of the hydrogen iodide formed during the reaction, or added to the solution, opposes itself to the complete addition of hypoiodous acid to the unsaturated linkings, and so reduces the absorption of iodine. H. C. R.

Oxidation of Lumbang and Linseed Oils and of the Principal Compounds in Lumbang Oil. A. P. West and A. I. de Leon (*Philippine J. Sci.*, 1924, **24**, 123—140).—When lumbang and linseed oils are blown under the same conditions at 75°, the percentage of apparent oxygen absorption, volatile products evolved, and total oxygen absorption in the early stages of oxidation are greater for lumbang than for linseed oil. As the oxidation process continues, the velocity of oxygen absorption increases more rapidly for linseed than for lumbang oil until after 100 hours the percentage of total oxygen absorption of linseed is greater than that of lumbang oil. Data giving the total percentage of oxygen absorption per hour during definite periods of time for these two oils indicate that for about the first 30 hours lumbang oil absorbs oxygen much more rapidly than does linseed oil. After 30 hours of oxidation, the rate of absorption of oxygen by lumbang oil gradually decreases, whilst the corresponding rate for linseed oil considerably increases. Both oils have about the same absorption velocity for oxygen for the period of oxidation extending from 30 to 40 hours. In the case of linseed oil, the velocity of oxygen absorption increases continually up to a period of 100 hours, beyond which the oxidation experiments were not continued. Both linseed and lumbang oils contain linolenic, linolic, and oleic glycerides, and also saturated glycerides. Linseed oil contains a much larger percentage of linolenic glycerides and of saturated glycerides than does lumbang oil. Possibly autocatalysts are formed in both these oils during oxidation and tend to accelerate the velocity of oxygen absorption, whilst the saturated glycerides present tend to retard the velocity of absorption. Constants of samples of lumbang and linseed oils blown for various periods of time at 75° were determined. Both oils gave very similar results. The surface tensions and refractive indices of both oils increased slightly on oxidation, whilst

the iodine values decreased considerably. Samples of lumbang oil oxidised for various periods of time were analysed. The percentage of oxidised glycerides increased, whilst the percentage of unoxidised unsaturated glycerides decreased. The linolenic glycerides of lumbang oil were oxidised more readily than the linolic and the linolic more readily than the oleic glycerides. H. C. R.

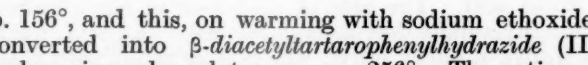
Quantitative Reduction by Hydriodic Acid of Halogenated Malonyl Derivatives. III. Mechanism of the Reaction. R. W. WEST (*J. Chem. Soc.*, 1924, **125**, 710—721).—The reaction between α-bromomalonyldimethylamide and hydriodic acid is bimolecular, and is probably indicated by the scheme ·CO·CHBr· → ·C(OH):Br· → ·CI(OH)·CHBr· → ·C(OH):CH+IBr (cf. Meyer, A., 1911, i, 350). The rate of reaction between hydriodic acid and αα′-dibromo-, αα′-chlorobromo-, and α-bromo-α′-alkylmalondimethylamides is independent of the concentration of the potassium iodide, but varies with that of the acid present, indicating that the primary (slow) reaction is the hydrolysis :CXBr+H_2O= :CXH+HOBr, which is followed by the instantaneous reduction of the hypobromous acid. The rate of reduction of the α-bromo-α′-alkylmalondimethylamides decreases in the order *iso*butyl (methyl), *n*-propyl, *iso*propyl, *n*-butyl, ethyl, which is identical with that for the rates of formation of the methylamides from the corresponding ethyl α-alkylmalonates. The effect is to be ascribed to steric hindrance rather than to polarity. The following α-alkylmalondimethylamides are obtained by heating the corresponding α-alkylmalonic ethyl esters with alcoholic monomethylamine at 100—140°: *α-methyl-*, colourless plates, m. p. 154°; *α-ethyl-*, small needles, m. p. 176°; α-n-*propyl-*, thin needles, m. p. 171°; α-iso*propyl-*, colourless needles, m. p. 167°; α-n-*butyl-*, colourless needles, m. p. 177°, and α-iso*butyl-malonodimethylamide*, thin needles, m. p. 163°. *α-Bromo-α′-methylmalonodimethylamide*, colourless needles, m. p. 114°, was prepared by brominating the above methyl derivative in chloroform, the following by brominating the corresponding α-alkylmalonodimethylamides in glacial acetic acid, all as colourless needles: *α-bromo-α′-ethyl-*, m. p. 136°; *α-bromo-α′*-n-*propyl-*, m. p. 106°; *α-bromo-α′*-iso*propyl-*, m. p. 101°; *α-bromo-α′*-n-*butyl-*, m. p. 89°, and *α-bromo-α′*-iso*butyl-malonodimethylamide*, m. p. 111°. F. G. W.

Action of Diacetyltartaric Anhydride and Chlorofumaryl Chloride on Aromatic Amines and Hydrazines. F. D. CHATTAWAY and G. D. PARKES (*J. Chem. Soc.*, 1924, **125**, 464—470).—Phenyliminosuccinanil (cf. T., 1923, **123**, 663) is obtained by the action of aniline on chlorofumaranilide at 150°. *Chloromaleinanil*, $\begin{matrix}CCl\cdot CO\\ \|\\ CH\cdot CO\end{matrix}>NPh$, small, colourless needles, m. p. 170°, is formed on heating the aniline salt of chloromaleic or chlorofumaric acid at 170—180°, and yields phenyliminosuccinanil on heating with aniline. *Chloromalein*-p-*chloroanil*, minute, glistening, irregular plates, m. p. 175°, and *chloromalein*-p-*bromoanil*, microcrystalline powder, m. p. 190°, are obtained similarly. *Chlorofumarodiamide*,

$CONH_2 \cdot CCl:CH \cdot CONH_2$, needles, m. p. 187°, *chlorofumaro-dimethylamide*, minute, colourless needles, m. p. 173°; *-di-*p*-chloroanilide*, clusters of pale yellow needles, m. p. 223°; and *-di-*p*-bromoanilide*, minute, faintly yellow needles, m. p. 236°, are obtained by the action of chlorofumaryl chloride on ammonia and the corresponding amines, respectively. The di-*p*-bromoanilide is also obtained by the action of bromine in glacial acetic acid on chlorofumarodianilide.

Aqueous potassium hydroxide hydrolyses phenyliminosuccinanil with formation of β-anilinoacrylic acid, whilst in alcohol the products are aniline, potassium oxalate, and potassium acetate.

Phenylhydrazine diacetyltartrate, a white, microcrystalline powder, melts partly at about 70° with loss of water and formation of *diacetyltartarophenylhydrazido-acid* (I), m. p. 168°, with formation of α-*diacetyltartarophenylhydrazide* (II), small, faintly yellow needles,



(I.) (II.) (III.)

m. p. 156°, and this, on warming with sodium ethoxide in alcohol, is converted into β-*diacetyltartarophenylhydrazide* (III), minute, colourless, irregular plates, m. p. 256°. The action of excess of phenylhydrazine on diacetyltartaric anhydride, or on the above α-hydrazide, affords tartarodiphenylhydrazide (T., 1903, **83**, 1349) and acetylphenylhydrazine. F. G. W.

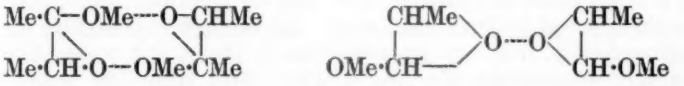
Formals of Primary Alcohols. M. Ghysels (*Bull. Soc. chim. Belg.*, 1924, **33**, 57—78).—Formals have been prepared by a direct distillation method from methyl, ethyl, *n*-propyl, *n*-butyl, *iso*butyl, and *n*-amyl alcohols. A non-volatile catalyst such as sulphuric acid or toluene-*p*-sulphonic acid is used which is eliminated immediately by the distillation. High yields of practically pure formals can be obtained in a single operation except in the cases of methylformal and ethylformal. Methylformal forms with the excess of alcohol an azeotropic mixture containing 92·15% of formal. Ethylformal gives a ternary azeotropic mixture with the excess of alcohol and the water produced in the reaction, from which it is separated by the addition of carbon disulphide; after separation of the aqueous layer and removal of the carbon disulphide, the ethylformal is obtained practically pure. *n*-Propylformal also yields a ternary azeotropic mixture with the excess of alcohol and water. All the formals prepared give binary azeotropic mixtures with water. The boiling points and approximate composition of these mixtures are given. R. B.

Glucosidic Acetals derived from Simple α- or β-Hydroxyketones and their Polymerisation. M. Bergmann and S. Ludewig (*Annalen*, 1924, **436**, 173—183; cf. Bergmann and Miekeley, A., 1921, i, 763; Fischer, A., 1895, i, 437).—The formation of glucosidic compounds from α- or β-hydroxy-aldehydes or -ketones has not previously been observed. The authors have shown that

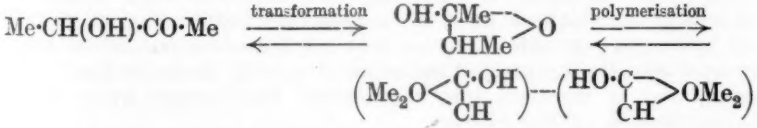
simple α-hydroxyketones, such as acetol, acetoin, and benzoylcarbinol, yield glucosidic *cyclo*acetals on treatment with methyl alcohol and hydrogen chloride, according to the scheme

$$R\cdot CO\cdot CHR'(OH) \longrightarrow \begin{matrix} CHR' \\ O\!\!-\!\!\!-\!\!\!> \\ \end{matrix} CR\cdot OMe.$$

These *cyclo*acetals polymerise easily, being bimolecular in solution and in the vapour phases at low pressures and temperatures; when strongly heated, they dissociate, but on cooling the bimolecular form is again obtained as crystals. This phenomenon is a property of an αβ-oxygen bridge in glucosides, but the three cases mentioned are peculiar, as in the gaseous state they are easily dissociated. The acetals of acetoin and glycollaldehyde are bimolecular over a comparatively wide range of temperature, whereas acetol*cyclo*acetal is dissociated at 100° under a pressure of a few millimetres. The derivatives of benzoylcarbinol cannot be examined owing to their high melting points. The following formulæ are suggested for dimeric acetoin*cyclo*acetal.



It is known that α-hydroxy-aldehydes and -ketones themselves polymerise to bimolecular forms, acetoin being an example. Refractometric measurements indicate that the unimolecular liquid form of acetoin possesses an alicyclic hydroxy-carbonyl structure. The change to the bimolecular crystalline form and the slow reverse change (at the ordinary temperature) indicate some structural alteration for which the following scheme is suggested:



Acetoin, b. p. 140—144°, d_4^{17} 0·9972, $n_D^{17\cdot3}$ 1·4190, is best prepared from γ-bromobutan-β-one by warming with an excess of potassium formate in dry methyl alcohol or with water and freshly precipitated calcium carbonate or potassium hydrogen carbonate. It is converted by acetic anhydride and pyridine into the acetate, b. p. 169—173°, $d_4^{16\cdot3}$ 1·038, $n_D^{16\cdot3}$ 1·4157.

Acetoin may be polymerised by the action of granulated zinc at −15° (cf. Diels and Stephan, A., 1907, i, 1000), when colourless crystals slowly separate, m. p. 83° (cf. von Pechmann and Dahl, A., 1890, 1234). Vapour density determinations in all cases were made by the method of Bleyer and Kohn, whence M=91 (req.=88) at 140°/2 mm. *Methyl*cyclo*acetal* was prepared from acetoin by the action of 1% methyl-alcoholic hydrogen chloride at 0°; bisacetoin may be employed (m. p. 73—73·5°, b. p. 196—198°/745 mm.). In phenol solution, it is bimolecular and also at 80°/0·8 mm., but

at higher temperatures the vapour dissociates and is unimolecular at 140°/2 mm.

Acetol methyl*cyclo*acetal (m. p. 127°), prepared from acetol by means of methyl-alcoholic hydrogen chloride, at 100°/10 mm. is partly bimolecular, but at 140°/1·5 mm. it is unimolecular.

Ethylglycoloside (cf. Bergmann and Miekeley, *loc. cit.*) is bimolecular at 140°/8 mm., and unimolecular at 180°/10 mm.

The methyl*cyclo*acetal of benzoylcarbinol, m. p. 192°, was unimolecular at 200°, but at higher temperatures some secondary changes took place which interfered with the accuracy of the measurements. A. E. C.

Isomerism of Thioaldehydes. E. Fromm and M. Soffner (*Ber.*, 1924, **57**, [*B*], 371—373).—A reply to Hinsberg (A., 1923, i, 1056; cf. Fromm and Schultis, A., 1923, i, 580).—The crude product (m. p. 216°) of the action of hydrogen sulphide on formaldehyde, whether freshly prepared or preserved during several months, loses hydrogen sulphide when treated with lead oxide and sodium hydroxide. It is converted into the substance, m. p. 247° (Hinsberg's β-trithioformaldehyde), not only by hydriodic acid, but also by concentrated hydrochloric acid; the change is therefore due to transformation and not to reduction. The sulphoxides derived from trithioformaldehyde, m. p. 216°, and from the substance, m. p. 247°, are probably identical; their solubilities are the same, and they yield the same product when treated with concentrated hydriodic acid.

The properties of the compound formed from hydrogen sulphide and formaldehyde appear to be in harmony with the formula $SH{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}S\ldots\ldots CH_2{\cdot}S{\cdot}CH_2{\cdot}SH$; the length of the chain cannot be determined, since there is no available method for the examination of the molecular weight of the compound. Oxidation of trithioformaldehyde or of the polymeric thioaldehyde, m. p. 247°, by hydrogen peroxide in acetic acid solution does not afford much insight into their constitution, since it is very probable that either compound is resolved into monomeric thioformaldehyde in the initial stages of the change.

α-Trithioformaldehyde, m. p. 216°, is the only compound of the group to which a definite molecular weight can be assigned. The degree of polymerisation of the product, m. p. 247°, cannot be ascertained, and it is purely arbitrary to regard it as a trimeride. H. W.

Formation of Acetone from Acetates. E. Häggland and E. O. Hedman (*J. pr. Chem.*, 1924, [ii], **107**, 50—64).—Dry distillation of sodium acetate at 400° in a current of steam gives nearly as high a yield of acetone as the distillation of calcium acetate; when inert gases such as nitrogen are used in place of steam, the yield of acetone is not raised in this way. Mixing the sodium acetate with calcium oxide or carbonate or sodium carbonate raises the yield of acetone considerably, and also accelerates the reaction, acetone formation being practically complete in the first hour instead of in 3—4 hours. This accelerating action was also observed

in an atmosphere of nitrogen. Rather more carbon monoxide and less carbon dioxide were produced than in the distillation of calcium acetate. Methane was only produced in quantity when sodium hydroxide was added to the sodium acetate; in this case very little acetone was produced. R. B.

Density and Viscosity of Acetone at Low Temperatures. E. H. ARCHIBALD and W. URE (*J. Chem. Soc.*, 1924, **125**, 726—731).—The following values were obtained for the density of acetone at the temperatures given: 0·0°, 0·8140; −10·0°, 0·8251; −20·0°, 0·8370; −30·0°, 0·8473; −40·0°, 0·8575; −50·0°, 0·8777; −70·0°, 0·8884; −80·0°, 0·9002; and −90·0°, 0·9117. Corresponding viscosities (absolute units) are: 0°, 0·00389; −10·6°, 0·00451; −20·4°, 0·00517; −30·3°, 0·00613; −40·0°, 0·00713; −49·9°, 0·00818; −59·7°, 0·00981; −69·7°, 0·01200; −79·7°, 0·01505; and −89·7°, 0·02051. The large increase in viscosity–temperature coefficient may account for the large conductivity–temperature coefficients found for solutions of organic substances in the liquid halogen hydrides. F. G. W.

Interaction of Tellurium Tetrachloride and the Higher β-Diketones. I. G. T. MORGAN and H. D. K. DREW (*J. Chem. Soc.*, 1924, **125**, 731—754).—The course of the reaction between tellurium tetrachloride and β-diketones, in chloroform or benzene, is determined by the complexity of the carbon chain of the diketone. If the solvent contains alcohol, the latter may enter into the reaction. The tellurium β-diketones, obtained by reducing the tellurium β-diketone dichlorides with potassium metabisulphite, are powerful bactericides (*Biochem. J.*, 1924, **18**, 190).

[With C. R. PORTER.]—*n*-Butyrylacetone yields, in pure chloroform, *tellurium* n-*butyrylacetone dichloride* (I), transparent, colourless prisms, m. p. 153—154° after darkening at 144°; in presence of alcohol, *tellurium* O-*ethyl*-n-*butyrylacetone trichloride* (III), golden-yellow needles, m. p. 105·5—106·5° (decomp.), is also formed.

(I.) $R\cdot C(\overset{\frown}{O})CH\cdot CO\cdot CH_2\cdot TeCl_2$ $\qquad$ $R\cdot C(\overset{\frown}{O})CH\cdot CO\cdot CH_2\cdot Te$ (II.)

$C_3H_7\cdot C(OEt):CH\cdot CO\cdot CH_2\cdot TeCl_3$ (III.) $\qquad$ $C_6H_{13}\cdot CO\cdot CH:C(OH)\cdot CH_2\cdot TeCl_3$ (IV.)

Tellurium n-*butyrylacetone*, $C_7H_{10}O_2Te$ (II), forms yellow needles, m. p. 110—112°. *n*-Heptoylacetone yields *tellurium* n-*heptoylacetone dichloride* (see I), nacreous, compact, or acicular prisms, m. p. 87°, and *tellurium* n-*heptoylacetone trichloride* (IV), colourless, nacreous, six-sided plates, m. p. 117° (decomp.). *Tellurium* n-*heptoylacetone*, $C_{10}H_{16}O_2Te$ (see II), forms yellow needles or golden-yellow scales, m. p. 86°, and shows residual acidity. The trichloride is not converted into the cyclic dichloride on boiling with pure chloroform, and addition of anhydrous aluminium chloride led to the formation of a crystalline aluminium derivative.

[With I. ACKERMAN.]—Dipropionylmethane yields *tellurium dipropionylmethane dichloride*, $C_7H_{10}O_2Cl_2Te$, thin, colourless, six-

sided plates (from acetone or benzene) darkening at 157°, and intumescing at 162°, or glistening prisms (from methyl alcohol), darkening at 150° and intumescing at 170° (cf. T., 1921, **119**, 616), and *tellurium* O-*ethylpropionylmethane trichloride*, $C_9H_{15}O_2Cl_3Te$, transparent, lemon-yellow prisms, m. p. 110—111° (decomp.). *Tellurium dipropionylmethane*, $C_7H_{10}O_2Te$, forms very tough, golden-yellow needles, m. p. 151° (decomp.), sublimes at 110° under reduced pressure, and shows no enolic reactions.

Tellurium propionyl-n-*butyrylmethane dichloride*, $C_8H_{12}O_2Cl_2Te$, forms silvery flakes, darkening at 150°, m. p. 156° (decomp.). *Tellurium propionyl*-n-*butyrylmethane*, $C_8H_{12}O_2Te$, forms yellow needles, m. p. 101—102° (decomp.). *iso*Butyrylacetone (b. p. 163°/752·5 mm.; *copper* salt, light blue, voluminous, crystalline powder, m. p. 167—168°) yields *tellurium* O-*ethyl*iso*butyrylacetone trichloride*, $C_9H_{15}O_2Cl_3Te$, pale yellow flakes or needles, m. p. 103° (decomp.). *iso*Valerylacetone (b. p. 183°/741 mm.; copper salt, m. p. 154°) yields *tellurium bis*iso*valerylacetone dichloride*,

$$C_{16}H_{26}O_4Cl_2Te,$$

transparent, colourless, acicular prisms, or nacreous leaflets, m. p. 97—98° (decomp.), and *tellurium* O-*ethyl*iso*valerylacetone trichloride*, small, compact, lemon-yellow, gem-like crystals, changing at 88° to a yellow glass having m. p. 101—102° (decomp.). *γ-Methylpropionylacetone* [*copper* salt, dark olive-green crystals, m. p. 174—176° (decomp.), or greenish-grey needles, m. p. 175—177° (decomp.)], yields *tellurium γ-methylpropionylacetone dichloride*, colourless, glistening prisms, m. p. 166—167° (decomp.) after sintering at 164°, which is reduced to the neutral *tellurium γ-methylpropionylacetone*, long, soft, pale golden needles, or elongated prisms, m. p. 125—126° (decomp.), subliming at 100° in a vacuum. *γ-Ethyl*-n-*butyrylacetone*, colourless, fragrant oil, b. p. 101—102°/9 mm. [*copper* salt, m. p. 166° (decomp.)], yields *tellurium γ-ethyl*-n-*butyrylacetone dichloride*, nacreous rosettes of colourless, prismatic needles, m. p. 140° (decomp.). *Tellurium γ-ethyl*-n-*butyrylacetone*,

$$C_9H_{14}O_2Te,$$

forms yellow needles, sintering at 110°, m. p. 113°, and is non-enolic.

Dipropionylethylmethane, $Et{\cdot}CH(CO{\cdot}Et)_2$, forms a colourless oil with a pleasant, slightly peppery odour, b. p. 105—106°/13 mm., 202—203°/744 mm. [*copper* salt, grey, microcrystals (from alcohol), m. p. 178—180°, or silver-grey needles (from benzene), m. p. 174—176°]. *Tellurium dipropionylethylmethane dichloride* forms colourless, transparent, six-sided prisms, darkening from 172°, m. p. 182° (decomp.), and is reduced to *tellurium dipropionylethylmethane*, tough, golden needles, m. p. 137—138° (decomp.), subliming at 110° in a vacuum. *Tellurium γγ-diethylacetylacetone dichloride* forms colourless, nacreous flakes or prisms, softening at 177°, m. p. 178·—180°. *Tellurium γγ-diethylacetylacetone* forms brittle, yellow, acicular needles, or needles with characteristically serrated edges, m. p. 85—86°, and has no residual acidity.

Diacetylacetone yields a mixture of *dimethylpyrone tellurichloride* (V), spear-like aggregates of golden-yellow needles, and the *oxy-*

chloride $[(C_7H_8O_2)H]_2TeOCl_4$, colourless crystals, m. p. 115°. Tetra-acetylethane yields a *substance* crystallising in pale golden, six-sided plates or needles, blackening at 135°, which is hydrolysed

(V.) $\left[O<\begin{matrix}CMe{:}CH\\CMe{:}CH\end{matrix}>C{:}O\ .\ .\ .\ H\right]_2<TeCl_6$;

$$\left[CH_2<\begin{matrix}CMe_2\text{-}CH_2\\C(OH){:}CH\end{matrix}>C{:}O\ .\ .\ .\ H\right]_2<TeCl_6;\quad \text{(VI.)}$$

with formation of 3 : 4-diacetyl-2 : 5-dimethylfuran, of which it is probably the tellurichloride. Dimethyldihydroresorcinol affords *dimethyldihydroresorcinol tellurichloride* (VI), large, transparent, pale yellow prisms, resinifying at 130°, m. p. 160—165° (decomp.). Ethyl acetoacetate yields *tellurium ethyl* O-*ethylacetoacetate trichloride* (*tellurium ethyl* β-*ethoxycrotonate trichloride*),

$$CO_2Et\cdot CH{:}C(OEt)\cdot CH_2\cdot TeCl_3,$$

colourless plates, softening at 88°, m. p. 90—92° (decomp. 140°). Definite products were not obtained by condensing tellurium tetrachloride with ethyl malonate, 3-allylacetylacetone, acetylmesityl oxide, acetylcamphor, ω-phenylacetylacetone, benzylidenebisacetylacetone (non-enolic and dienolic forms) and 2-acetyl*cyclo*hexanone). The benzeneazo-β-diketones yield bright yellow, stable compounds containing tellurium and halogen. F. G. W.

Interaction of Tellurium Tetrachloride and the Higher β-Diketones. II. G. T. Morgan and R. W. Thomason (*J. Chem. Soc.*, 1924, **125**, 754—759).—*Dibutyrylmethane*,

$$CH_2(CO\cdot C_3H_7)_2,$$

is obtained as a fragrant, colourless liquid, b. p. 204—205°, by the condensation of methyl propyl ketone with *n*-butyl *n*-butyrate or (in better yield) with ethyl *n*-butyrate. It forms a blue *copper* salt, m. p. 156°, and condenses with *p*-nitrophenylhydrazine to form 1-p-*nitrophenyl*-3 : 5-*di*-n-*propylpyrazole*, $C_{15}H_{19}O_2N_3$, yellowish-brown needles, m. p. 53°. It condenses with tellurium tetrachloride in chloroform with formation of *tellurium dibutyrylmethane dichloride* (I), vitreous needles (from methyl alcohol), m. p. 148°, or colourless needles (from alcohol or chloroform–petroleum), m. p. 120—139° or 138—139°, and *tellurium dibutyrylmethane trichloride*, $Pr^{\alpha}CO\cdot CH{:}C(OH)\cdot CHEt\cdot TeCl_3$ or $Pr^{\alpha}C(OH){:}CH\cdot CO\cdot CHEt\cdot TeCl_3$, large, tabular crystals, m. p. 87—88°, with blackening. Both forms of the dichloride are reduced, with alkali hydrogen sulphite, to *tellurium dibutyrylmethane* (II), golden-yellow needles, m. p. 97°.

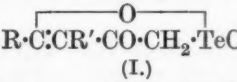
(I.) $Pr^{\alpha}C{:}CH\cdot CO\cdot CHEt\cdot TeCl_2$ (O-bridged) $\qquad$ $Pr^{\alpha}C{:}CH\cdot CO\cdot CHEt\cdot Te$ (O-bridged) (II.)

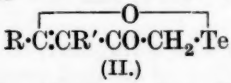
γ-*Ethylpropionylacetone*, $C_2H_5\cdot CO\cdot CHEt\cdot CO\cdot CH_3$, obtained by the action of ethyl iodide on sodium propionylacetone, forms a fragrant oil, b. p. 192—193°/755 mm. (*copper* salt, m. p. 176°). *Tellurium* γ-*ethylpropionylacetone dichloride*, $C_8H_{12}O_2Cl_2Te$, acicular prisms, m. p. 167° (decomp.), and *tellurium* γ-*ethylpropionylacetone*, $C_8H_{12}O_2Te$, pale yellow needles, m. p. 109°, are described.

γ-n-*Propylacetylacetone* was obtained as a fragrant oil, b. p.

191—192°/745 mm. (*copper* salt, m. p. 215°), by the action of *n*-propyl iodide on sodium acetylacetone at 180° under pressure (cf. T., 1920, **117**, 780). *Tellurium* γ-n-*propylacetylacetone dichloride*, $C_8H_{12}O_2Cl_2Te$, forms colourless, acicular prisms, m. p. (indefinite) 180°. *Tellurium* γ-n-*propylacetylacetone*, $C_8H_{12}O_2Te$, forms pale yellow needles, m. p. 106—107°. γ-iso*Propylacetylacetone*, prepared similarly to the *n*-propyl derivative, b. p. 182—183°/745 mm., has an odour of dry hay. It does not form a copper salt, and gives no coloration with ferric chloride. *Tellurium* γ-iso*propylacetylacetone dichloride* forms lustrous, colourless, acicular prisms, blackening indefinitely at about 150°. *Tellurium* γ-iso*propylacetylacetone* forms yellow needles, m. p. 152—153°. F. G. W.

Interaction of Tellurium Tetrachloride and the Higher β-Diketones. III. G. T. Morgan and E. Holmes (*J. Chem. Soc.*, 1924, **125**, 760—765).—The isolation of the condensation products of tellurium tetrachloride and the β-diketones is rendered more difficult, as the series is ascended, by their increasing fusibility and solubility in organic media. n-*Valerylacetone*, a pungent oil, b. p. 194° (blue *copper* salt, m. p. 143°), is converted by tellurium tetrachloride into *tellurium* n-*valerylacetone dichloride*, $C_8H_{12}O_2Cl_2Te$ (R=*n*-C_4H_9, R′=H, in formula I), colourless needles, m. p. 125°; this is reduced by potassium metabisulphite to *tellurium* n-*valerylacetone*, $C_8H_{12}O_2Te$ (see II), yellow needles, m. p. 80°. *n*-Hexoylacetone (blue *copper* salt, m. p. 138°) gives *tellurium* n-*hexoylacetone dichloride* (R=*n*-C_5H_{11}, R′=H, in I), colourless


(I.)


(II.)

needles, m. p. 102°. *Tellurium* n-*hexoylacetone* (see II) forms brilliant yellow needles, m. p. 86°.

γ-n-*Butylacetylacetone*, b. p. 210—212°/750 mm. (grey *copper* salt, m. p. 186°) was prepared by the action of *n*-butyl iodide on sodium acetylacetone. *Tellurium* γ-n-*butylacetylacetone dichloride* (R=CH_3, R′=*n*-C_4H_9, in I), lustrous, colourless crystals, m. p. 155°, is reduced to *tellurium* γ-n-*butylacetylacetone* (see II), primrose-yellow needles, m. p. 129°. γ-n-*Butylpropionylacetylacetone*, similarly obtained from propionylacetone, has b. p. 223—224°/745 mm. (*copper* salt, grey needles, m. p. 156°). *Tellurium* γ-n-*butylpropionylacetone dichloride* (R=C_2H_5, R′=*n*-C_4H_9, in I), forms colourless leaflets, m. p. 103°. *Tellurium* γ-n-*butylpropionylacetone* (see II) forms golden-yellow needles, m. p. 93°. Methyl *n*-nonyl ketone was condensed with ethyl acetate and sodium to form n-*decoylacetone*, an oil with a sweet, penetrating odour, b. p. 276°/760 mm. (*copper* salt, pale blue needles, m. p. 114°). *Tellurium* n-*decoylacetone dichloride* (R=*n*-C_9H_{19}, R′=H, in I), forms grey crystals, m. p. 49°, and *tellurium* n-*decoylacetone* (see II), yellow needles, m. p. 64°. F. G. W.

Bactericidal Action of the Tellurium Derivatives of Aliphatic β-Diketones. II. G. T. Morgan, E. A. Cooper, and A. W. Burtt.—(See i, 591.)

Pentosans. VII. Fusion of Xylan with Potassium Hydroxide. E. HEUSER and J. ROTH (*J. pr. Chem.*, 1924, [ii], **107**, 1—6; cf. A., 1923, i, 1061, 1181).—Fusion of xylan with 10 parts of potassium hydroxide and an equal weight of water for ½ hour to 2 hours gives oxalic, acetic, and formic acids in amounts depending on the temperature. Oxalic acid is formed most readily at 220—250° (yield 53%), with some evolution of hydrogen. Below 200° much xylan remains unchanged. The yields of acetic acid and formic acid at 230—280° vary from 13—15% and 9—12%, respectively. The presence of succinic acid has been proved, but its amount could not be determined. Succinic acid is not formed in the fusion and subsequently decomposed, for this acid was recovered practically unchanged after fusion with potassium hydroxide. Traces of pyrocatechol and protocatechuic acid have been detected, but the presence of these and other aromatic substances is attributed to the presence of impurities in the xylan. The amount of formic acid produced leads to the conclusion that the oxalic acid results from decomposition of the formate, as in the fusion of cellulose, a conclusion which was confirmed by measuring the hydrogen evolved when the fusion was conducted in a stream of nitrogen. R. B.

Mutarotation of the Sugars. R. GILMOUR (*J. Chem. Soc.*, 1924, **125**, 705—706).—A question of priority (cf. Gilmour, P., 1909, **25**, 225; Baker, Ingold, and Thorpe, this vol., i, 262). F. G. W.

Chemical Effects of γ-Rays of Radium. A. SLOSSE (*Compt. rend. Soc. Biol.*, 1923, **89**, 96—98; from *Chem. Zentr.*, 1924, i, 33—34).—The effect of the radiations from radium bromide enclosed in a sealed tube and immersed in a solution of pure dextrose was to produce a small decrease in optical activity, attributed to a partial transformation of β- into γ-dextrose. The presence of formaldehyde was established; no other degradation products of dextrose were found. After subjection to radiation, the dextrose solution became much more readily oxidisable by potassium permanganate and sulphuric acid. G. W. R.

Glucose [Dextrose] from α- and β-Glucosides. H. COLIN and [MLLE.] A. CHAUDUN (*Compt. rend.*, 1924, **178**, 779—782).—The hydrolysis of α- and β-methyl-, of α- and β-ethyl-glucosides, and of salicin, has been followed polarimetrically and by copper titration. Salicin hydrolyses initially to give a glucose of low rotatory power (increasing with time) and is therefore a β-glucoside. E. E. T.

Acetone-sugars and their Derivatives. I. The Constitution of Glucosediacetone [Di*iso*propylidene-glucose] and a new Benzoylglucosemonoacetone. H. OHLE (*Ber.*, 1924, **57**, [*B*], 403—409).—The action of aniline hydrochloride on benzoylglucosediacetone (Fischer and Noth, A., 1918, i, 226) in boiling, absolute alcoholic solution leads to the formation of a second

benzoylglucosemonoacetone, $CMe_2{:}C_6H_9O_5{\cdot}OBz$, $[\alpha]_D^{20}$ −26° in alcoholic solution, which could not be caused to crystallise. In so far as hydrolysis does not occur, it is stable towards dilute acids, but is rapidly converted by traces of alkali into the crystalline benzoylglucosemonoacetone of Fischer and Noth (*loc. cit.*). The constitution of the new derivative has not been established completely, but it is considered to be the primary product of the action from which Fischer's compound is obtained by isomerisation. Since Fischer, Pfähler, and Brauns (A., 1920, i, 840) have shown that the wandering of acyl groups occurs from the secondary to the primary alcoholic hydroxy group, it is assumed that the crystalline product is ζ-benzoylglucosemonoacetone. This hypothesis is supported by the observations that it is the sole isolable product of the action of benzoyl chloride on glucosemonoacetone in the presence of pyridine, and that both benzoylglucosemonoacetones are convertible into the same tribenzoylglucosemonoacetone, the experimental conditions being such that isomerisation is excluded.

Glucosemonoacetone reacts with acetone to form glucosediacetone as readily in the presence of anhydrous copper sulphate as in that of hydrogen chloride. A similarly ready reaction is observed in the cases of glycerol and of glyceryl α-benzoate.

It is suggested that the wandering of acyl and alkyl groups is more frequent than has been assumed previously in the chemistry of the sugars. The discordant results obtained by Irvine and Patterson (T., 1922, **121**, 2146) and by Levene and Meyer (A., 1923, i, 92) by the oxidation of methylglucosediacetone are probably attributable to this cause. H. W.

Crystallisation of Sucrose. J. A. KUCHARENKO (*Louisiana Planter*, 1923, **71**, 211—213, 231—232).—The concentration of supersaturated solutions of sucrose at the instant of crystallisation was determined at various temperatures; by the correlation of surface, S, and weight, P, in the equation $S^3=kP^2$, the rate of crystallisation of solutions of various degrees of supersaturation could be accurately measured. The speed of crystallisation was found to vary directly with the degree of supersaturation and with the temperature employed. CHEMICAL ABSTRACTS.

The System Maltose–Water. J. GILLIS (*Rec. trav. chim.*, 1924, **43**, 135—143).—The author has studied the lowering of the melting point of ice for high concentrations of maltose both in pure water and in the presence of ammonia. The resulting curve is shown together with the solubility curve of maltose between 0° and 96·5°. From the latter, the inference is drawn that the monohydrate of β-maltose exists as the solid phase in equilibrium with the solution up to the neighbourhood of 100°. The solubility curve is compared with the curves of lactose (Gillis, A., 1921, i, 11) and of dextrose (Jackson and Silsbee, A., 1922, i, 986). H. J. E.

Acetobromomaltose. H. FISCHER and F. KÖGL (*Annalen*, 1924, **436**, 219—228; cf. E. and H. Fischer, A., 1910, i, 716; Karrer, A., 1921, i, 310, 313, 768).—The authors question the

purity of the acetobromomaltose obtained by Karrer's method, as from this specimen a yield of only 30% of hepta-acetylmaltose is obtainable, whereas from their specimen a 70% yield is produced. Further, the acetobromomaltose obtained by Karrer's method has a very high bromine content, which indicates that some secondary reaction has taken place. Pure acetobromomaltose is prepared by allowing maltose to stand with acetyl bromide for 20—40 minutes at 0°; it is an amorphous solid which after 7 months' drying gave $[\alpha]_D^{15\cdot5}$ +171·5° in chloroform. Hepta-acetylmaltose, microscopic needles, m. p. 174—175°, was obtained by the action of sodium acetate and acetic acid on the bromo compound, the total yield being 70%. The specific rotation increased to a constant value on preservation, and, after 48 hours, is $[\alpha]_D^{10}$ +103·01° in *s*-tetrachloroethane.

Hepta-acetylbenzylmaltoside, colourless prisms, m. p. 125°, $[\alpha]_D^{16\cdot5}$ +27·76° in *s*-tetrachloroethane, was prepared from an absolute ethereal solution of the bromo compound by shaking with silver carbonate and benzyl alcohol. It is hydrolysed by methyl-alcoholic ammonia at 0° to *benzylmaltoside*, m. p. 147—148°, $[\alpha]_D^{17}$ +47·64° in aqueous solution.

Hepta-acetylethylmaltoside, prepared in the same way as the benzyl derivative, crystallises in prisms, m. p. 132°, $[\alpha]_D^{14}$ +48·93° in *s*-tetrachloroethane. It is hydrolysed to *ethylmaltoside*, m. p. 168—169°.

Hepta-acetylmethylmaltoside, m. p. 130—131°, is prepared in the same manner as the ethyl homologue. *Hexa-acetylmaltal* is obtained by the reduction of a solution of the acetobromomaltose in 50% acetic acid by zinc dust at 10°; it crystallises in colourless prisms. m. p. 134°, $[\alpha]_D^{16\cdot5}$ +64·15°. It adds on one atomic proportion of bromine in chloroform solution and on warming with water loses one acetyl group, leaving the penta-acetyl derivative as fine needles, m. p. 123°. This on acetylation with acetic anhydride and pyridine gives a substance, m. p. 113—114°, which has not been further examined. A. E. C.

Lactosan. A. PICTET and M. M. EGAN (*Helv. Chim. Acta*, 1924, **7**, 295—297).—When lactose is carefully heated at 120—130° at 4—6 mm., it loses its water of crystallisation, and at 185° in 10 to 12 hours it is converted into the anhydride, *lactosan*, $C_{12}H_{20}O_{10}$, a white, amorphous powder, m. p. 200—202° (decomp.), $[\alpha]_D$ +65·5—66·0°, without mutarotation. It is readily soluble in water, and its reducing power in terms of Fehling's solution is 61% of that of dextrose. Brewer's yeast does not ferment it. With phenylhydrazine, it gives the osazone of lactose, and when acetylated it gives octa-acetyl-lactose. Lactosan is polymerised by heating at 105°/15 mm. for ¼ hour with a trace of zinc chloride, forming a *tetralactosan*, $(C_{12}H_{20}O_{10})_4$, m. p. 245—246° (decomp.), which does not reduce Fehling's solution. By fuming hydrochloric acid, lactosan is partly converted into lactosyl chloride. The properties of lactosan indicate that it is ε-galactosylglucosan.

E. H. R.

Degradation of Starch by Salts. W. S. Iljin (*Biochem. Z.*, 1924, **145**, 14—17; cf. also Iljin, A., 1923, i, 172; Haehn, A., 1923, i, 443; Biedermann, A., 1923, i, 665).—Further experiments are described in which starch in dilute solution is hydrolysed by various concentrations of sodium, lithium, and calcium chlorides without the intervention of an enzyme. Potassium, magnesium, and barium chlorides are said to give similar results. J. P.

Action of Weak Bases on Cellulose Nitrate. G. G. Giannini (*Gazzetta*, 1924, **54**, 79—85).—Determinations of the compositions and of the molecular weights in freezing acetic acid exhibited by two preparations of the product obtained by Angeli by the action of pyridine on cellulose nitrate (A., 1919, i, 196; 1922, i, 922) containing, respectively, 8·98% and 10·08% N, as well as analyses of the gaseous mixtures emitted during their preparation, suggest that pyridine produces in cellulose nitrate a gradual denitration varying in velocity with the temperature. T. H. P.

Triphenylmethyl Ethers of Cellulose and Starch. B. Helferich and H. Koester (*Ber.*, 1924, **57**, [*B*], 587—591; cf. A., 1923, i, 331).—Cellulose, preferably in the form of material which has been regenerated from the xanthate (1 part), is converted by triphenylmethyl chloride (6 parts) and pyridine (14 parts) at 100° during 14—32 hours into *cellulose triphenylmethyl ether*, $C_{25}H_{24}O_5$, a pale pink, voluminous powder, m. p. about 260° (decomp.), which swells in contact with many organic media and gives colloidal solutions in pyridine, chloroform, and bromoform. Further prolongation of the reaction or use of a larger excess of triphenylmethyl chloride does not lead to the etherification of more hydroxyl groups. The ether is readily hydrolysed by hydrogen chloride in chloroform solution, yielding triphenylmethyl chloride (or the carbinol if water is present) and a carbohydrate which is identical analytically with the original material. If triphenylmethylcellulose is heated with acetic anhydride and pyridine on the water-bath, approximately one acetyl group is introduced into each dextrose component; with chloroacetyl chloride and pyridine, esterification takes place to a greater extent. Rice starch yields *starch triphenylmethyl ether*, $C_{25}H_{24}O_5$, which closely resembles the corresponding cellulose ether. H. W.

Adsorption of Aluminium Hydroxide from Aluminium Sulphate Solutions by Cotton and Wood Cellulose. C. G. Schwalbe (*Z. angew. Chem.*, 1924, **37**, 125—128).—The contradictions which occur in the literature as to whether aluminium hydroxide is adsorbed from aluminium sulphate solutions by cotton and wood cellulose are ascribed to the fact that the adsorptive power of fibres is conditioned by a large number of variable factors such as the period and temperature of steeping, the concentration of the solution in which the fibre is steeped, and especially the previous history of the fibre, circumstances which have an important effect on the nature of its surface. Cotton cellulose which had been stored for 7 years in a dry place failed to adsorb aluminium

from solutions of the sulphate or acetate or from sodium aluminate even after milling for 7 hours in a ball mill. In order to study the effects of the presence of hydrocellulose and oxycellulose, strips of cotton fabric were treated with 3% sulphuric acid and heated for 4 hours at 70°, and others were over-bleached before being used in adsorption experiments. The ash content of the samples so treated was found to increase very appreciably after steeping in an aluminium sulphate solution and subsequent washing. It is uncertain whether this increase in the adsorptive power of the fabric is due to the presence of hydrocellulose and oxycellulose or to a change in the nature and extent of the surface. Sized wood cellulose pulp is capable of adsorbing much greater quantities of aluminium hydroxide than the undamaged fibres, and the adsorptive power increases with the fineness of comminution up to a certain point, and thereafter remains approximately constant. The swelling of wood cellulose fibres exerts a great influence on their power of adsorbing aluminium hydroxide. The number of factors which affect the adsorptive power of wood cellulose is even greater than in the case of cotton cellulose, owing to the varying quantities of pentosans and hexosans which may be present. H. C. R.

Quantitative Determination of the Fluorescent Powers (the Spectro-fluorescometry) of Cellulose and its Derivatives. IV. S. J. Lewis (*J. Soc. Dyers and Col.*, 1924, **40**, 111—114).—A continuation of work previously described (this vol., i, 374). No essential differences were found in the fluorescent properties of yarn and ribbon prepared from the same solution of viscose, of hydrocellulose prepared by the action of sulphuric or hydrochloric acid on cotton linters, or of oxycellulose prepared by means of a hypochlorite or potassium permanganate. Experiments with cellulose tendered, by means of acids and exposure to daylight, indicate that changes in fluorescent power appear to be more noticeable in the region of λ 2900. Paper, after exposure for 3 weeks to radium, showed no fluorescence. It is again concluded that the physical condition of the material has but little effect on its fluorescent properties. A. J. H.

Polysaccharides. XXV. Methylation Products of Reserve Cellulose (Lichenin). P. Karrer and K. Nishida (*Helv. Chim. Acta*, 1924, **7**, 363—370).—Continuing previous work (this vol., i, 373), fresh evidence is put forward confirming the chemical similarity between lichenin or reserve cellulose and structural cellulose. Exhaustive methylation of lichenin gives a product containing 41·9% of methoxyl, compared with a maximum of 42—43% in the case of cotton. Methylated lichenin dissolves in cold water to a colloidal solution which coagulates on warming. In some respects, it resembles methylated hydrocellulose more than methylated cellulose, but, unlike the former, it does not depress the freezing point of water. The methylated lichenin, when heated with 1% methyl-alcoholic hydrogen chloride, gives trimethyl- and dimethyl-methylglucosides in similar proportions to those obtained from fully methylated cellulose by Irvine and Hirst (T., 1923, **123**,

529). The yield of trimethylglucose obtained by hydrolysis of the glucoside is smaller, however, than the 85% obtained by Irvine and Hirst. E. H. R.

Galegine. E. Späth and S. Prokopp (*Ber.*, 1924, **57**, [*B*], 474—480; cf. Tanret, A., 1914, i, 859).—Galegine is converted by hydrogen in the presence of palladised charcoal to *dihydrogalegine*, $CHMe_2{\cdot}[CH_2]_2{\cdot}N{:}C(NH_2)_2$, the constitution of which is deduced from its conversion by barium hydroxide into carbamide and *iso*amylamine and its synthesis from *iso*amylamine and cyanamide. Since galegine on oxidation with permanganate yielded acetone but no trace either of formaldehyde or *iso*butaldehyde, it must have the composition $CMe_2{:}CH{\cdot}CH_2{\cdot}N{:}C(NH_2)_2$ (cf. Barger and White, this vol., i, 272). An improved method for the isolation of galegine is described, consisting essentially in extracting the free base from its aqueous solution by means of amyl alcohol. Dihydrogalegine sulphate, white crystals, the *picrate*, yellow crystals, m. p. 173—174°, and m-*nitrobenzoyl* derivative of *iso*amylamine, m. p. 81—82°, are described. F. A. M.

Composition of Japanese Petroleum. I. S. Komatsu and S. Kusumoto (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 77—84).—The fraction of petroleum from Nishiyama, Echigo, distilling below 90°, is shown to consist mainly of methyl*cyclo*pentane, b. p. 71—72°, d_4^{25} 0·7295, n_D^{25} 1·3965, and *cyclo*hexane, b. p. 80—81°, d_4^{25} 0·765, n_D^{25} 1·414. [Cf. *B.*, 1924, 408.] W. A. S.

The Hydrogenating, Reducing, and Oxidising Action of Hydrazine on Organic Compounds. E. Müller and H. Kraemer-Willenberg (*Ber.*, 1924, **57**, [*B*], 575—583).—Benzyl alcohol reacts with 2 mols. of nearly anhydrous hydrazine at 180° to give nitrogen and toluene; if 4 mols. of hydrazine are used, hexahydrotoluene is obtained. At 280° benzene gives *cyclo*hexane, together with a small proportion of adipic acid (the requisite oxygen is derived from the trace of water present in the hydrazine). Toluene, *o*-, *m*-, and *p*-xylenes, mesitylene, and cymene are similarly transformed into their hexahydro-derivatives, hydrogenation occurring under milder experimental conditions with respect to temperature and duration as the number of carbon atoms in the hydrocarbon molecule increases. Pyridine and quinoline are not affected by hydrazine at any temperature up to 330°. Hydrobenzoin yields diphenylethylene oxide, m. p. 56°.

Monohydric phenols are not hydrogenated by hydrazine. At 100°, phenol gives the compound $(Ph{\cdot}OH)_2,N_2H_4$, m. p. 63°, which is unchanged by hydrazine at 200°. *p*-Cresol and *s*-xylenol yield similar *salts*, the *p*-cresol compound forming colourless needles, m. p. 61—62°. Polyhydric phenols are oxidised by hydrazine, as is evidenced by the copious formation of ammonia. *Quinol hydrazine*, $C_6H_{10}O_2N_2$, long, colourless needles, m. p. 154°, and resorcinol yield solid, nitrogenous products the constitution of which could not be elucidated.

Ethylene glycol is reduced by hydrazine at 200° to ethyl alcohol.

Glycerol is transformed into methyl alcohol, formic, acetic, and racemic acids. Erythritol yields oxalic acid, whereas dulcitol gives a hexose which is converted by phenylhydrazine into an osazone, $C_{18}H_{22}O_4N_4$, pale yellow needles, m. p. 205°. *d*-Mannitol yields dextrose. Cellulose is oxidised by hydrazine. H. W.

The System *cyclo*Hexane–Aniline. E. H. BUCHNER and D. KLEYN (*Rec. trav. chim.*, 1924, **43**, 153—157).—The critical temperatures of mixtures of *cyclo*hexane and aniline containing up to 40·1% of the latter were determined. The curve is regular and on extrapolation gives 427° as the critical temperature of aniline (cf. Guye and Malet, A., 1902, ii, 302). As no maximum was observed, the system is regarded as an exception to the general rule, and doubt is cast on the conclusions drawn by Buchner (A., 1918, ii, 9) in another case. The mutual solubilities of the two substances were also investigated; above 31·3°, there is complete miscibility in all proportions. H. J. E.

Catalytic Preparation of Amines. E. BRINER, P. FERRERO, and E. DE LUSERNA (*Helv. Chim. Acta*, 1924, **7**, 282—294).—Attempts were made to obtain aniline (i) by passing a mixture of benzene and ammonia vapours over a heated catalyst, (ii) from phenol and ammonia in a similar manner. From benzene and ammonia only traces of aniline could be obtained under any conditions; the observations of Wibaut are therefore confirmed (A., 1917, i, 386). The result is only to be expected, as the reaction is endothermic, $C_6H_6+NH_3=NH_2Ph+H_2-23{\cdot}6$ Cal. The second reaction gives appreciable yields of aniline, up to 12% of the theoretical, the best results being obtained using alumina as catalyst at 420°, with excess of ammonia and prolonged contact. The reaction in this case is exothermic, $PhOH+NH_3=NH_2Ph+H_2O+0{\cdot}4$ cal. With thoria as the catalyst, only traces of aniline are obtained, but appreciable quantities of diphenyl ether and phenylene oxide; these products are obtained also in absence of ammonia. When methyl alcohol mixed with phenol and ammonia vapours is passed over heated alumina, a mixture of methyl- and dimethylanilines is obtained, the former predominating, but the yields are smaller than those from phenol and ammonia alone. In presence of thoria some anisole is formed. E. H. R.

Freezing-point Curves for the System 2-Chloroacetanilide–4-Chloroacetanilide. K. J. P. ORTON and G. OWEN (*J. Chem. Soc.*, 1924, **125**, 766—767).—Owen's method (*J. Chem. Soc.*, 1923, **123**, 3393) has been applied to an examination of the freezing-point curves for the system 2-chloroacetanilide–4-chloroacetanilide. The results were in harmony with the behaviour of the system 2 : 4-dichloroacetanilide–4-chloroacetanilide, the lower-melting polymorph of 4-chloroacetanilide previously observed (*J. Chem. Soc.*, 1909, **95**, 1059) never separating from the liquid mixture in bulk but only when small quantities were cooled very slowly in capillary tubes. R. B.

Action of Hydrogen Chloride on a Dry Solution of a Chloroamine. F. G. SOPER (*J. Chem. Soc.*, 1924, **125**, 768—769).—The action of dry hydrogen chloride on a solution of 2 : 4-dichloro-*N*-chloroacetanilide in glacial acetic acid gives no trace of chlorine except in presence of moisture. This result suggests that hydrolysis, $:NCl+H_2O \rightleftharpoons :NH+HOCl$, is the first step in the production of chlorine and that the appearance of this gas is due to a subsequent interaction, $HCl+HOCl \rightleftharpoons Cl_2+H_2O$. R. B.

Solubility of Anilinesulphonic Acids. J. C. PHILIP and R. S. COLBORNE (*J. Chem. Soc.*, 1924, **125**, 492—500).—The solubility relations previously found to obtain between sulphanilic acid and water (*J. Chem. Soc.*, 1913, **103**, 284) have now been found to be characteristic of the anilinesulphonic acids generally. A notable feature of these acids is the readiness with which they form supersaturated solutions, from which under suitable conditions unstable hydrates may readily be produced. Solubility determinations show that these hydrates are not stable at any temperature on the solubility curve, but are either completely labile or are metastable over a small temperature range in the neighbourhood of 0°. Aniline-*o*-sulphonic acid forms a *monohydrate*, stable below 13·5°; above this temperature, the anhydrous acid is the stable solid phase. Aniline-*m*-sulphonic acid forms a sesquihydrate which separates below 20° as a metastable phase, with a greater solubility than that of the anhydrous acid. *p*-Bromoaniline-*o*-sulphonic acid gives, below 30°, a monohydrate which is metastable with respect to the anhydrous acid even at 0°, although its solubility can be readily measured up to 25°. *p*-Bromoaniline-*m*-sulphonic acid exists in two enantiotropic forms, the rhombic, stable above 100°, the monoclinic, stable at the ordinary temperature, and separation of the metastable monohydrate furnishes the most striking example of the class. This hydrate separates as a felted mass of crystals, which only slowly changes to the less soluble anhydrous acid. *p*-Chloroaniline-*o*-sulphonic acid with water at 0° slowly changes to a stable monohydrate, but no unstable hydrate was observed. *p*-Chloroaniline-*m*-sulphonic acid at 0° forms small tablets of a metastable monohydrate. R. B.

Chemotherapeutical Researches in the Series 205 Baeyer. Carbamates of the Aminobenzoylaminonaphthalenesulphonic Acids. E. FOURNEAU, J. TRÉFOUËL, (MME.) J. TRÉFOUËL, and J. VALLÉE (*Ann. Inst. Pasteur*, 1924, **38**, 81—114).—A more detailed account of work already noted (this vol., i, 382).

Absorption Spectra of some Derivatives of Phenol and other Substances. J. E. PURVIS.—(See this vol., ii, 219.)

Fluorescence Spectra. II. Phenol and Phenolic Ether Vapours. J. K. MARSH.—(See this vol., ii, 219.)

Action of the Oxides and the Oxy-acids of Nitrogen on Diphenyl Ether. H. RYAN and P. T. DRUMM (*Sci. Proc. Roy. Dubl. Soc.*, 1924, **17**, 313—320).—Diphenyl ether treated with

nitrogen peroxide alone or in carbon tetrachloride solution, or with nitrous fumes in the same solvent, gave a mixture of *op'*- and *pp'*-dinitrodiphenyl ethers (cf. Mailhe and Murat, A., 1912, i, 346; 1913, i, 44), with some 2 : 4-dinitrophenol; with nitrous fumes in acetic acid solution, the main product was the *p*-mononitro derivative. The latter was also formed when the ether was treated with nitric acid (*d* 1·4) either alone or in carbon tetrachloride or acetic acid. With fuming nitric acid (*d* 1·5) a mixture of the *pp'*-dinitro- and 2 : 2′ : 4 : 4′-*tetranitro-diphenyl ether*, m. p. 195°, was formed. This derivative was also obtained from 2 : 4-dinitrochlorobenzene and 2 : 4-dinitrophenol and by further nitration of 2 : 4-dinitrodiphenyl ether and of 2 : 4 : 4′-trinitrodiphenyl ether (cf. Cook, A., 1910, i, 731). 2 : 4 : 6-Trinitrodiphenyl ether (from picryl chloride and potassium phenoxide) and the 2 : 4 : 6 : 2′-tetranitro compound (prepared in a similar way) both gave on further nitration 2 : 4 : 6 : 2′ : 4′-*pentanitrodiphenyl ether*, colourless needles, m. p. 210°. W. A. S.

Action of the Oxides and the Oxy-acids of Nitrogen on Phenyl Benzyl Ether. H. Ryan and J. Keane (*Sci. Proc. Roy. Dubl. Soc.*, 1924, **17**, 287—295).—Treatment of phenyl benzyl ether in the cold, and for a long time if necessary, with nitrogen peroxide, gaseous or in carbon tetrachloride solution, with nitrous fumes or with nitric acid, alone or in carbon tetrachloride solution (cf. A., 1919, i, 13; 1923, i, 323), gave mostly *p*-nitrophenyl benzyl ether, a little *p*-nitrophenyl *p*-nitrobenzyl ether (cf. Kumpf, A., 1884, 1005), and varying amounts of decomposition products. Nitration seemed not to proceed with nitric acid in acetic acid or ether solution. Further nitration of *p*-nitrophenyl benzyl ether was brought about by treatment with nitric acid in carbon tetrachloride solution, but again not in acetic acid or alcohol. The product was the above dinitro derivative. With nitric acid alone, a mixture of o-p-*dinitrophenyl* p-*nitrobenzyl ether*, colourless prisms, m. p. 207—208°, and o-p-*dinitrophenyl* o-*nitrobenzyl ether*, needles, m. p. 188°, was formed. These compounds were also obtained by treating *o*-nitrophenyl benzyl ether in a similar way. Both trinitro derivatives were converted by the action of a mixture of fuming sulphuric and nitric acids into the same product, viz. o-o-p-*trinitrophenyl* o-p-*dinitrobenzyl ether*, scales, m. p. 146°. An attempt to prepare a hexanitro derivative of the ether resulted only in the isolation of a decomposition *product*, m. p. 139—140°. W. A. S.

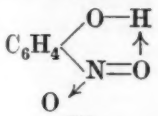
Action of the Oxides and the Oxy-acids of Nitrogen on Diphenyl Ethylene Ether. H. Ryan and T. Kenny (*Sci. Proc. Roy. Dubl. Soc.*, 1924, **17**, 305—311).—Diphenyl ethylene ether, $Ph{\cdot}O{\cdot}C_2H_4{\cdot}O{\cdot}Ph$, treated with gaseous nitrogen peroxide, or nitrogen peroxide in carbon tetrachloride solution, or with nitric acid (*d* 1·5), alone or in carbon tetrachloride solution, gave mostly the *pp'*-dinitro derivative, m. p. 143° (cf. Weddige, A., 1881, 1136), accompanied by 2 : 4-dinitrophenol and decomposition products. Nitration did not take place with nitric acid dissolved in acetic acid. *Phenyl* o-*nitrophenyl ethylene ether*, rectangular plates, m. p.

97°, and the corresponding p-*nitro* derivative, prisms, m. p. 86°, were prepared by interaction of the corresponding potassium nitrophenoxide and ω-bromophenetole. Di-*o*-nitrophenyl ethylene ether was prepared similarly (Weddige, *loc. cit.*). From the *o*-nitro and this di-*o*-nitro derivative, by further nitration, o-*nitrophenyl* o-p-*dinitrophenyl ethylene ether*, m. p. 172°, was obtained. All these lower nitrated derivatives gave ultimately *di*-2 : 4-*dinitrophenyl ethylene ether*, pale yellow, flat prisms, m. p. 214°, and continued action of nitric acid destroyed the molecule. o-*Nitrophenyl* p-*nitrophenyl ethylene ether*, rectangular prisms, m. p. 117·5°, was also prepared synthetically. W. A. S.

Solubility of the Aminophenols. N. V. Sidgwick and R. K. Callow (*J. Chem. Soc.*, 1924, **125**, 522—527).—As regards solubility in water and benzene, the aminophenols are an abnormal group, their abnormality resembling that of the phenylenediamines (*Chem. Soc. Trans.*, 1923, **123**, 2817) rather than the usual type. The *o*-compound is less soluble in water than the *p*-isomeride; in benzene, the solubilities are about the same. The *m*-compound is more soluble in water and less soluble in benzene than either of its isomerides. *m*-Aminophenol very readily forms supersaturated solutions in water, consequently it was possible to follow the two-liquid curve up to 60—70° below the saturation point, and even to measure the metastable ice curve in dilute solutions. This appears to be a general property of *m*-derivatives (cf. *Chem. Soc. Trans.*, 1922, **121**, 2256). The following boiling points were determined at 11 mm. pressure: *m*-aminophenol, 164° (with very slight decomp.); *p*-aminophenol, 174° (after melting with decomp.). *o*-Aminophenol sublimes rapidly at 153°. (Cf. following abstract.) R. B.

Abnormal Benzene Derivatives. N. V. Sidgwick and R. K. Callow (*J. Chem. Soc.*, 1924, **125**, 527—538).—The results of a series of investigations (*Chem. Soc. Trans.*, 1915, **107**, 1202; 1920, **117**, 389, 396; 1921, **119**, 979, 1001, 1013; 1922, **121**, 1844, 1853, 2256, 2263, 2586; 1923, **123**, 2813, 2819, and preceding abstract) on the volatility and solubility in the liquid state of certain classes of benzene derivatives are summarised and a possible explanation of the phenomena is discussed. The benzene derivatives in question are described as abnormal because the isomerides differ widely in their vapour pressures and solubility relations. Such abnormality depends on the presence in the molecule of two active or alterable substituents (OH, CO_2H, NH_2, CHO, NO_2, Cl, etc., as opposed to unalterable such as the alkyls) and of these two, one must be OH, NH_2 (or substituted NH_2), or CO_2H. Apparently one group makes the compound sensitive and the other augments this sensitiveness. The relations holding among the substituted phenols differ in many respects from those observed with the amines and acids, which again differ from one another. Among the phenols, abnormality was found in all cases examined where the second substituent was other than alkyl. The meta- and para-compounds resemble one another closely as normal isomerides, but differ markedly from the ortho-compounds in being (*a*) less volatile,

(*b*) more miscible with water, and (*c*) less miscible with benzene, properties characteristic of polar as opposed to non-polar substances. Consideration of other properties confirms the view that the ortho-series is abnormal and from the fact that in these compounds the polar character due to the hydroxylic hydrogen is suppressed in much the same way as if this hydrogen were replaced by methyl, the suggestion is put forward of a co-ordinate linking of the phenolic hydrogen with some atom of the second group. This is expressed in the annexed formulæ, in which the arrow (→) points to the atom receiving the two unshared electrons. These formulæ represent the most stable type of chelate ring known, and formula (II) explains the abnormality of the hydroxybenzoic acids, their esters and aldehydes (X=OH, OAlk, or H). With other active groups (halogens, OH, OAlk, and perhaps NH_2), a five-atom ring must be assumed, $C_6H_4<^{Cl}_{O}>H$ or $C_6H_4<^{O}_{O}>H$, which is less common, but occurs in the cupferron compounds and is possible in a large class of mordant dyes. Such chelate compounds always tend to be non-polar (cf. acetylacetones) and this ring structure explains why *o*-nitrophenol cannot form compounds with aniline, *p*-toluidine, benzamide, and acetamide, whereas the *m*- and *p*-nitrophenols can; and why if the phenol has an active substituent both in the ortho- and in the para-positions, the influence of the ortho-group predominates and the compound is non-polar. An explanation is also afforded of Auwers' conclusion (A., 1903, ii, 268) that a substituent group which when occupying the ortho-position in a solute gives abnormality, for example, in benzene solution, when introduced into the solvent tends to reduce the abnormality. The behaviour of abnormal derivatives other than phenol is much less easy to explain, and co-ordination through the hydrogen atom is only one of several possibilities. With the chloro- and nitro-acids, the difference between meta- and para-compounds is as great as that between the meta- and ortho-, whilst solubilities both in water and in benzene are in the order $o>m>p$. The amino-compounds are somewhat less abnormal, and this is probably connected with their basicity. The introduction of an acetyl group into the chloro- and nitro-anilines tends to increase the abnormality. Among the amino-compounds the meta-derivative occupies an exceptional position, being less volatile than the para-derivative, and its solubility both in benzene and in water is much nearer to (and sometimes less than) the ortho- than is the case with the other classes of abnormal benzene derivatives, a distinction which points to direct chemical influence rather than to either ring-formation or steric effect. R. B.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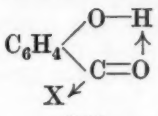
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Action of the Oxides and Oxy-acids of Nitrogen on β-Naphthyl Ethyl Ether. H. Ryan and J. Keane (*Sci. Proc. Roy. Dubl. Soc.*, 1924, **17**, 297—303).—β-Naphthyl ethyl ether on

treatment with nitrogen peroxide, nitrous fumes, or nitric acid in glacial acetic acid or carbon tetrachloride solution, gave mainly 1-nitro-2-naphthyl ethyl ether, and with gaseous nitrogen peroxide or nitric acid (more than before) in carbon tetrachloride solution or alone, a mixture of 1 : 6- and 1 : 8-dinitro-2-naphthyl ethyl ether. The ether itself, its 1-nitro-, 1 : 6-dinitro-, and 1 : 8-dinitro-derivatives were all converted by the further action of nitric acid into 1 : 6 : 8-*trinitro-2-naphthyl ethyl ether*, colourless prisms or scales, m. p. 189—190° (cf. Staedel, A., 1883, 863), the constitution of which was thus proved. Heated with alcoholic ammonia, it gave 1 : 6 : 8-trinitro-β-naphthylamine, m. p. 300—301°. W. A. S.

Conversion of Eugenol into *iso*Eugenol. S. K. Gokhale, J. J. Sudborough, and H. E. Watson (*J. Indian Inst. Sci.*, 1923, **6**, 241—255).—The composition of mixtures of eugenol and *iso*eugenol is best estimated from the refractive index. The earlier method (McKie, *Chem. Soc. Trans.*, 1921, **119**, 777) is troublesome and untrustworthy. Eugenol has n_D^{30} 1·53664 and *iso*eugenol n_D^{30} 1·57237. The curve showing the relationship between composition and refractive index for mixtures is a straight line. The temperature coefficient of the refractive index is about 0·0004 per degree for both substances.

When eugenol is fused with sodium hydroxide at 200—210°, little if any conversion and much decomposition takes place; with potassium hydroxide (4 parts), 85% of the theoretical yield of *iso*eugenol is obtained (cf. Einhorn and Frey, A., 1894, i, 578). A mixture of 2 parts of sodium hydroxide and 1 part of potassium hydroxide also gives a good yield. When eugenol is heated with 6 to 8 parts of 50% potassium hydroxide solution in an autoclave at 170—180°, almost complete conversion takes place. W. A. S.

Adrenaline Compounds. C. Funk and L. Freedman (U. S. Pat. 1472298).—β-*Methylamino*-4-α-*ethoxyethylpyrocatechol hydrochloride*, thin, rectangular prisms, m. p. 169°, is prepared by heating *r*-adrenaline (or its hydrochloride) for several hours in a reflux apparatus with absolute ethyl alcohol containing dry hydrogen chloride equivalent to 1—4 mols. of adrenaline, and cooling. A *substance* (*hydrochloride*, rectangular prisms, m. p. 180—183°), possibly a lactonic compound of 2 mols. of adrenaline, is also formed.

Chemical Abstracts.

Properties of Neighbouring Hydroxy Groups Attached to a Benzene Nucleus. R. L. Alimchandani (*J. Chem. Soc.*, 1924, **125**, 539—543).—The hypothesis that the carbon atoms of the benzene nucleus are charged alternately positively and negatively finds support in the properties of the three vicinal methoxy groups of 3 : 4 : 5-trimethoxy-2-trichloromethylphthalide and 3 : 4 : 5-trimethoxybenzenesulphonic acid. When chloral hydrate is condensed with 3 : 4 : 5-trimethoxybenzoic acid by means of 90% sulphuric acid, the product consists mainly of 3 : 4 : 5-trimethoxy-2-trichloromethylphthalide, rectangular plates, m. p. 76—77°,

from which the simultaneously formed 4-hydroxy-3 : 5-dimethoxy-2-trichloromethylphthalide is separated by means of dilute sodium hydroxide. The trimethoxyphthalide by treatment with 98% sulphuric acid is converted into 4-hydroxy-3 : 5-dimethoxy-2-trichloromethylphthalide, m. p. 172—173°, and with sodium hydroxide into 3 : 4 : 5-trimethoxyphthalide-2-carboxylic acid, m. p. 147—149°. Hydrolysis of this acid with 96—98% sulphuric acid gives 4-hydroxy-3 : 5-dimethoxyphthalide-2-carboxylic acid. 3 : 4 : 5-Trimethoxyphthalide similarly yields 4-hydroxy-3 : 5-dimethoxyphthalide, m. p. 144°. The action of 96—98% sulphuric acid on pyrogallyl trimethyl ether gives in varying proportions 3 : 4 : 5-*trimethoxybenzenesulphonic acid*, leaflets, containing $1{\cdot}5H_2O$, m. p. 95—97° (the *barium*, *sodium*, and potassium salts are described), and 4-*hydroxy*-3 : 5-*dimethoxybenzenesulphonic acid*, leaflets, $1{\cdot}5H_2O$, m. p. 128—129° (the *barium* and sodium salts are described), which is not hydrolysed by sulphuric acid even in hot solution and on oxidation yields 2 : 6-dimethoxy-*p*-benzoquinone. Treatment with bromine gives 1 : 2 : 3-*tribromo*-5-*hydroxy*-4 : 6-*dimethoxybenzene*, slender prisms, m. p. 134—135°, which by methylation with methyl sulphate gives 1 : 2 : 3-tribromo-4 : 5 : 6-trimethoxybenzene, prisms, m. p. 75—76°. This compound was also obtained by the action of bromine on 3 : 4 : 5-trimethoxybenzenesulphonic acid, the sulphonic group being displaced. Hydrolysis of the trimethoxybenzenesulphonic acid to pyrogallyl trimethyl ether readily takes place in hot sulphuric acid. R. B.

Methyl Ether of Diphenylphenylacetylenylcarbinol. K. ZIEGLER and K. TRIPP (*Ber.*, 1924, **57**, [*B*], 420; cf. A., 1923, i, 921).—The carbinol is readily methylated by dissolving it in hot methyl alcohol and adding 1 to 2% of sulphuric acid, previously diluted with methyl alcohol. On cooling, the methyl ether crystallises out almost quantitatively, and after recrystallisation forms leaflets, m. p. 123—124°. It is decomposed by acids to give phenyl β-phenylstyryl ketone, m. p. 86—87° (cf. A., 1922, i, 556). F. A. M.

Benzeins. R. MEYER and W. GERLOFF (*Ber.*, 1924, **57**, [*B*], 591—599; cf. A., 1923, i, 230).—Benzaurin dissolves in aqueous alkali to an intense carmine solution which gradually fades; the fading is not due to atmospheric action as suggested by Doebner (*Ber.*, 1879, **12**, 1464), but probably to the transformation of coloured *p*-hydroxyfuchsone into colourless dihydroxytriphenylcarbinol. On passing carbon dioxide into the colourless solution, the original benzaurin is reprecipitated. It is considered to be *p*-hydroxyfuchsone hydrate, $OH{\cdot}C_6H_4{\cdot}CPh{:}C_6H_4{:}O,H_2O$. Benzaurin forms a crystalline *bisulphite* compound, $(OH{\cdot}C_6H_4)_2C(Ph)SO_3Na$, which decomposes on keeping. It was not found possible to prepare an oxime, phenylhydrazone, or semicarbazone. Treatment of an alkaline solution of benzaurin with potassium cyanide gave the *nitrile*, $(OH{\cdot}C_6H_4)_2C(Ph)CN$, an oil which slowly solidified to crystals, m. p. 203—204°; attempts to hydrolyse the nitrile to the corresponding dihydroxytriphenylmethanecarboxylic acid were unsuccessful. On treatment with acetic anhydride, the nitrile

yielded a *diacetyl* derivative, colourless crystals, m. p. 140—141°, and on benzoylation gave *dihydroxytriphenylmethanecarboxylamide dibenzoate*, $(OBz{\cdot}C_6H_4)_2C(Ph)CONH_2$; on hydrolysing this with alcoholic potassium hydroxide and acidifying the resultant solution, the original nitrile was recovered. *Benzaurin diethyl ether* and *dibenzyl ether* are colourless, crystalline substances melting at 75—76° and 110°, respectively. Bromination of benzaurin in acetic acid in presence of iron gives *tetrabromobenzaurin*, dark red crystals which lose no water on moderate heating (*sodium* salt, brown needles with green iridescence). Benzaurin is reduced by alcoholic ammonia to *pp'*-diaminotriphenylmethane; using strong aqueous ammonia, *p*-aminofuchsonimine is formed.

Resorcinolbenzein dried in a vacuum has the formula $C_{19}H_{14}O_4$. At 140°, it loses 1 mol. of water, leaving a product, $C_{19}H_{12}O_3$, as found by Kehrmann; the authors therefore give the hydrated substance the formula $OH{\cdot}C_6H_3<\overset{O}{\underset{CPh}{\rangle}}C_6H_3{\cdot}O \ldots H_2O$. The following derivatives of resorcinolbenzein were prepared: *diacetate*, yellow needles, m. p. 145°; *dibenzoate*, colourless needles, m. p. 152°; dibromo derivative, reddish-yellow powder which loses H_2O at 140°; tetrabromo derivative, crystals which lose 1 mol. of HBr at 140—150°; *pentabromo* derivative, brown needles, which sublime with decomposition at 140—150° (*sodium salt*, brownish-red needles with green iridescence). *Dinitroresorcinolbenzein nitrate*, obtained by warming the benzein with strong nitric acid, forms a brilliant red, crystalline powder which decomposes with a slight explosion on heating. F. A. M.

Insecticides. II. Constitution of Chrysanthemum-mono- and -di-carboxylic Acids. H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, **7**, 201—211).—Three acids were obtained by hydrolysis of the semicarbazones of the active constituents of insect powder (cf. p. 523). The first, chrysanthemumcarboxylic acid, $C_{10}H_{16}O_2$, is readily separated from the others on account of its volatility in steam, and is shown to be 2 : 2-*dimethyl*-3-iso*butenyl*cyclo*propane*-1-*carboxylic acid*, $CMe_2{:}CH{\cdot}CH<\overset{CMe_2}{\underset{CH{\cdot}CO_2H}{|}}$, $[\alpha]_D^{20}$ +20·1°. Its *methyl* ester is a colourless liquid, b. p. 99°/14 mm., 86—87°/10 mm., $[\alpha]_D^{20}$ +20·74°, having a faint odour of insect powder; *chloride*, $C_{10}H_{15}OCl$, colourless oil, b. p. 85°/12 mm., 58°/0·03 mm.; *anilide*, white needles, m. p. 101°; *amide*, white needles, m. p. 131°; *anhydride*, viscous oil, b. p. 125°/15 mm. When reduced by the Paal-Skita method, the acid takes up two atoms of hydrogen, giving 2 : 2-*dimethyl*-3-iso*butyl*cyclo*propane*-1-*carboxylic acid*, a colourless, mobile oil, b. p. 124—126°/10 mm. Its *chloride* has b. p. 89—90°/12 mm.; *amide*, white crystals, m. p. 132—132·5°; and *anilide*, large, colourless crystals, m. p. 82—83°. *Methyl* l-trans-*caronate*, $C_9H_{14}O_4$, obtained by decomposing chrysanthemumcarboxylic acid ozonide, forms a mass of white crystals, m. p. 37—38°, b. p. 93°/25 mm., $[\alpha]_D$ −8·26° in benzene. The second acid obtained from insect powder, chrys-

anthemumdicarboxylic acid, has the composition $C_{10}H_{14}O_4$, and the third, $C_{11}H_{16}O_4$, is its monomethyl ester. It is the latter which is present in the active constituent of the insect powder, the former being formed from it by hydrolysis. By the action of ozone, the second acid gives *l-trans*-caronic acid and pyruvic acid, whilst the third gives *l-trans*-caronic acid and methyl pyruvate. Chrysanthemumdicarboxylic acid is therefore 2 : 2-*dimethyl*-3-β-*carboxypropenyl*cyclo*propane*-1-*carboxylic acid*,

$$CO_2H\cdot CMe{:}CH\cdot CH\!<\!\begin{matrix}CH{:}CO_2H\\ |\\ CMe_2\end{matrix};$$

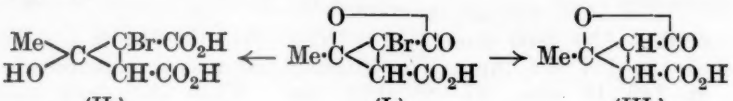
it has $[\alpha]_D^{17}$ +72·8°. The *chloride*, $C_{10}H_{12}O_2Cl_2$, forms white crystals, m. p. 48—50°, b. p. 151°/12 mm.; *anilide*, m. p. 204—205°. The *monomethyl* ester, $CO_2H\cdot\begin{matrix}CMe_2\\ |\\ CH\end{matrix}\!>\!CH\cdot CH{:}CMe\cdot CO_2Me$, is a viscous oil, b. p. 129—130°/0·03 mm., $[\alpha]_D^{18}$ +103·9°; the *chloride* is a colour-oil, b. p. 114°/0·5 mm. The *dimethyl* ester is a colourless oil, b. p. 149°/16 mm., 87—88°/0·25 mm. When chrysanthemum-dicarboxylic acid is distilled at atmospheric pressure, it partly decomposes into carbon dioxide and 2 : 2-*dimethyl*-3-*propenyl*-cyclo*propane*-1-*carboxylic acid*, a mobile oil, b. p. 133°/12 mm.; *chloride*, b. p. 95°/12 mm. With pyrethrolone, this acid forms an ester having weak insecticidal properties. The ester obtained from reduced chrysanthemumcarboxylic acid and pyrethrolone is inactive. E. H. R.

3-Methyl*cyclo*propene-1 : 2-dicarboxylic Acid. F. Feist (*Annalen*, 1924, **436**, 125—153; cf. Feist, A., 1893, i, 404; Goss, Ingold, and Thorpe, *J. Chem. Soc.*, 1923, **123**, 327).—When bromo-*iso*dehydracetic acid is treated with alkali, an acid (A) is produced, m. p. 200°, which on dibromination and reduction with sodium amalgam yields an isomeride (B), m. p. 189°. Only one formula is possible for both these isomeric methyl*cyclo*propenedicarboxylic acids, namely, $CMe\!<\!\begin{matrix}CH\cdot CO_2H\\ |\\ C\cdot CO_2H\end{matrix}$, since both are racemic acids which can be resolved into their optically active components. The acid A (*silver* salt, and *phenylhydrazine* salt, white needles, m. p. 138°) was resolved by means of its quinine salt into *d*- and *l*-acids having the rotations $[\alpha]_D$ +215° and −156°. They both melt at 200°. The methyl ester, needles, m. p. 32°, has b. p. 122°/20 mm., d_4^{20} 1·142, n_D^{20} 1·4672. The ethyl ester, m. p. 38°, b. p. 135°/15 mm., the *anilide*, white powder, m. p. 246°, and *carbamide* salt, m. p. 215°, are described.

The acid B was resolved by means of its brucine and quinine salts; the extreme values obtained for the *d*- and *l*-acids were $[\alpha]_D$ +179·8° and −118°. The methyl ester of B has m. p. 30·5° and b. p. 116°/20 mm.; d_4^{20} 1·140, n_D^{20} 1·4669. It is not identical with the methyl ester of A and on hydrolysis regenerates B. The latter is converted into A by concentrated sulphuric acid or by heating with concentrated alkali.

By dibromination of the acids or their esters and subsequent reduction with sodium amalgam, B is produced. The dibromo-

acid derived from A melts at 244° and gives an *ethyl* ester, b. p. 183—184°/13 mm., d_4^{20} 1·590, n_D^{20} 1·5026. The *methyl* ester forms white needles, m. p. 77°. The dibromo-acid derived from B melts at 232° and yields an *ethyl* ester, b. p. 177°/13 mm., d_4^{20} 1·566, n_D^{20} 1·500. This dibromo-acid on warming with water or concentrated alkali yields a monobasic lactonic acid, $C_6H_5O_4Br$, m. p. 171°, 2-*bromo*-3-*hydroxy*-3-*methyl*cyclo*propane*-1 : 3-*dicarboxylolactonic acid* (I), which is readily transformed by alkali into the corresponding hydroxy-acid, $C_6H_7O_5Br$ (II). The *methyl* ester of the lactonic acid has m. p. 98°, b. p. 166°/15 mm. By reduction of the lactonic acid with sodium amalgam, bromine is removed and the lactone of so-called oxalbutyric acid, m. p. 140—141°, is left (III).



(II.) (I.) (III.)

The lactonic acid (m. p. 171°) is identical with the lactone of so-called oxalbromobutyric acid. On oxidation with alkaline permanganate, it yields a tribasic *acid*, $C_6H_5O_6Br$ (m. p. 225°), which gives a *dimethyl* ester, m. p. 76°.

Reduction of 3-methyl*cyclo*propene-1 : 2-dicarboxylic acids (A or B) by means of colloidal palladium and hydrogen yields two isomeric 3-methyl*cyclo*propane-1 : 2-dicarboxylic acids (m. p. 147° and 108°). A third isomeride, m. p. 138—140°, has also been obtained as a by-product in the reduction of the dibromomethyl*cyclo*propane-dicarboxylic acid by means of sodium amalgam. Of the three possible isomerides, two have been already described, one, m. p. 108°, by Preiswerk (A., 1903, i, 459), and the other by Kötz and Stalmann (A., 1903, i, 741), who isolated a syrup. The acid, m. p. 147°, is thought to be the *trans* acid, as it gives no anhydride. The methyl ester has b. p. 208·5—209°/760 mm., 100°/14 mm., and on hydrolysis yields an acid, m. p. 138°. The acid, m. p. 147°, after exposure to moisture melts at 138°, but after drying its melting point rises to 147°. Acid A gives an *ozonide*, $C_6H_6O_7$ (horny solid), which on hydrolysis yields oxalic and acetic acids, through acetyloxalacetic acid. The methyl ester gives an *ozonide* (colourless oil) which on hydrolysis yields methyl acetoacetate and methyl oxalacetate. A. E. C.

Anhydrides. W. Autenrieth and G. Thomae. (See i, 485).

Constitution of Sparassol. A. St. Pfau (*Ber.*, 1924, **57**, [*B*], 468—470).—The product, m. p. 67—68° (sparassol), obtained by Wedekind and Fleischer (this vol., i, 174) from the fungus *Sparassis ramosa*, is proved to be identical with a product obtained by Pfau from a fungus, *Evernia prunastri*. It is identical with the methyl ester of everninic acid, 6-hydroxy-4-methoxy-*o*-toluic acid, and is not methyl 4-hydroxy-6-methoxy-*o*-toluate as suggested by Wede-

kind and Fleischer. Sparassol does not exist as such in the fungus, but is formed by the alcoholysis of the evernic acid present. On hydrolysis with 10% aqueous sodium hydroxide, sparassol yields everninic acid. F. A. M.

Sparassol. E. Späth and K. Jeschki (*Ber.*, 1924, **57**, [*B*], 471–474; cf. preceding abstract).—The constitution of sparassol was proved in the following manner. Orcinol was converted into orcylaldehyde by the method of Gattermann and Köbner (A., 1899, i, 363) and this into orsellinic acid (4 : 6-dihydroxy-*o*-toluic acid). The last was methylated by means of diazomethane to the 4-methyl ether of methyl orsellinate (methyl everninate), which melted at 67—68° and was identical with Wedekind and Fleischer's sparassol. The *acetyl* derivative (*acetylsparassol*) has m. p. 63—64°. The *dimethyl* ether of methyl orsellinate has m. p. 41—42°, and the *nitro* derivative of methyl everninate, m. p. 168—169°. F. A. M.

Physical Constants of Stereoisomeric Compounds. K. von Auwers and B. Ottens (*Ber.*, 1924, **57**, [*B*], 437—446).—Systematic investigation of the benzenoid hydrocarbons (cf. A., 1916, i, 130; 1919, i, 578) and of derivatives of *cyclo*hexane (A., 1920, i, 721) has shown that the propinquity of side chains or other substituents to one another causes an increase in density and index of refraction and a decrease in molecular refractivity. It is to be expected, therefore, that the *cis*-forms of stereoisomeric compounds as a consequence of the closer juxtaposition of their substituents would resemble the ortho- or 1 : 2-derivatives and have a higher density and refractive index but a lower molecular refraction than their *trans*-isomerides. This hypothesis has already been utilised to some extent in the elucidation of the configuration of compounds (cf. Skita, A., 1920, i, 27; 1923, i, 671; Hückel, this vol., i, 31); its general validity is now tested by an examination of several well-defined pairs of isomerides.

Ethyl hexahydrophthalate and ethyl 4-amino-2 : 6 : 6-trimethylhexahydrobenzoate exhibit well-marked differences which are in harmony with the rule mentioned above; with the ethyl esters of hexahydroterephthalic and hexahydrohomophthalic acids, the differences are so slight as to be inconclusive, whilst with the ethyl hexahydro*iso*phthalates the slight differences are contrary to the rule. The latter observation, combined with the experience of Skita (A., 1923, i, 671), indicates that for the present physical data cannot be regarded as trustworthy aids in elucidating the configuration of meta- or 1 : 3-derivatives. The values observed with trithioaldehyde and trithioacetone are in harmony with those which are anticipated; this is also the case with the isomeric $\beta\epsilon$-dihydroxy-$\beta\epsilon$-dimethyl-Δ^{γ}-hexenes, $OH\cdot CMe_2\cdot CH{:}CH\cdot CMe_2\cdot OH$ (cf. Zalkind, A., 1923, i, 176). The stereoisomeric dimethylsuccinic and dimethylglutaric esters show similar small, scarcely utilisable differences in their constants such as are observed with the hydrogenated tere- and homo-phthalic esters. The further accumulation of methyl groups in the succinic molecule produces the expected effects. The physical constants of pairs of stereoisomeric alkyl-

glutaconic esters are very similar. This is to be expected if Feist's view that these substances are geometrical isomerides is accepted, since marked differences in the spectroscopic constants are only observed with simple, stereoisomeric acids and esters of the acrylic series, and these tend to disappear as the molecule becomes more complicated, even to only a limited extent. On the other hand, exaltations such as would be expected if Thorpe's formulation is adopted are not observed.

Physical constants are recorded for the following compounds. *Ethyl* cis-*hexahydrophthalate*, b. p. 133°/10 mm., d_4^{20} 1·054, $n_\alpha^{13\cdot9}$ 1·45296, n_{He}^{20} 1·453. *Ethyl* trans-*hexahydrophthalate*, b. p. 135°/11 mm., d_4^{20} 1·040, n_{He}^{20} 1·450. *Ethyl* cis-*hexahydroisophthalate*, b. p. 142°/11 mm., d_4^{20} 1·045, n_{He}^{20} 1·452. *Ethyl* trans-*hexahydroisophthalate*, b. p. 142°/12 mm., d_4^{20} 1·047, n_{He}^{20} 1·453. *Ethyl* cis-*hexahydroterephthalate*, b. p. 151°/13 mm., $d_4^{20\cdot6}$ 1·0516, $n_{He}^{20\cdot6}$ 1·45222. *Ethyl* trans-*hexahydroterephthalate*, lustrous, flattened needles, m. p. 43—44°, $d_4^{64\cdot4}$ 1·0105, $n_{He}^{64\cdot4}$ 1·43367. *Ethyl* cis-*hexahydrohomophthalate*, b. p. 273°, d_4^{20} 1·040, n_{He}^{20} 1·454. *Ethyl* trans-*hexahydrohomophthalate*, b. p. 275°, d_4^{20} 1·038, n_{He}^{20} 1·453. Ethyl *cis*-4-amino-2 : 6 : 6-trimethylhexahydrobenzoate, b. p. 127°/11 mm., d_4^{20} 0·990, n_{He}^{20} 1·475. Ethyl *trans*-4-amino-2 : 6 : 6-trimethylhexahydrobenzoate, b. p. 127°/11 mm., d_4^{20} 0·980, n_{He}^{20} 1·473.

Ethyl succinate, b. p. 217°, d_4^{20} 1·041, n_{He}^{20} 1·420. Ethyl methylsuccinate, b. p. 218°, d_4^{20} 1·011, n_{He}^{20} 1·419. Ethyl *cis*-αβ-dimethylsuccinate, b. p. 221°, d_4^{20} 0·996, n_{He}^{20} 1·423. Ethyl *trans*-αβ-dimethylsuccinate, b. p. 220°, d_4^{20} 0·995, n_{He}^{20} 1·421. Ethyl αα-dimethylsuccinate, b. p. 218°, d_4^{20} 0·993, n_{He}^{20} 1·421. *Ethyl trimethylsuccinate*, b. p. 226°, d_4^{20} 0·993, n_{He}^{20} 1·436. Ethyl tetramethylsuccinate, b. p. 219°, d_4^{20} 0·995, n_{He}^{20} 1·436. *Ethyl* cis-αγ-*dimethylglutarate*, b. p. 231°, d_4^{20} 0·980, n_{He}^{20} 1·423. *Ethyl* trans-αγ-*dimethylglutarate*, b. p. 231°, d_4^{20} 0·977, n_{He}^{20} 1·422.

Ethyl *cis*-β-methylglutaconate, b. p. 131°/19 mm., d_4^{20} 1·034, n_{He}^{20} 1·452. Ethyl *trans*-β-methylglutaconate, b. p. 127°/12 mm., d_4^{20} 1·034, n_{He}^{20} 1·452. Ethyl *cis*-αβ-dimethylglutaconate, b. p. 128°/13 mm., d_4^{20} 1·024, n_{He}^{20} 1·454. Ethyl *trans*-αβ-dimethylglutaconate, b. p. 125°/12 mm., d_4^{20} 1·031, n_{He}^{20} 1·454. Ethyl *cis*-α-ethyl-β-methylglutaconate, b. p. 127°/12 mm., d_4^{20} 1·019, n_{He}^{20} 1·455. Ethyl *trans*-α-ethyl-β-methylglutaconate, b. p. 139°/18 mm., d_4^{20} 1·014, n_{He}^{20} 1·453.

Trithioacetone, $C_9H_{18}S_3$, has m. p. 22°, d_4^{20} 1·068, n_{He}^{20} 1·542. *cis*-Trithioacetaldehyde, m. p. 101°, and *trans*-trithioacetaldehyde, m. p. 126°, in addition to trithioacetone have been examined in quinoline solution; the solvent is shown to be suitable for this purpose.

cis-βε-Dihydroxy-βε-dimethylhexene, m. p. 76°, d_4^{99} 0·869, n_{He}^{99} 1·423. *trans*-βε-Dihydroxy-βε-dimethylhexene, m. p. 69°, d_4^{99} 0·864, n_{He}^{99} 1·422. H. W.

Synthesis of Polyhydroxyphenylalanines. F. Schaaf and A. Labouchère (*Helv. Chim. Acta*, 1924, **7**, 357—363).—For the synthesis of 2 : 5-dihydroxyphenylalanine, gentisaldehyde dimethyl

ether (2 : 5-dimethoxybenzaldehyde) was condensed with hippuric acid, and the resulting α-benzoylamino-2 : 5-dimethoxycinnamic acid reduced to α-benzoylamino-2 : 5-dimethoxy-β-phenylpropionic acid, from which the 2 : 5-dihydroxyphenylalanine was obtained. This method was inapplicable for the synthesis of trihydroxyphenylalanine as the cinnamic acid derivative could not be reduced. The following method was, however, successful. 2 : 3 : 4-*Trimethoxybenzaldehyde* was obtained by Gattermann's synthesis from pyrogallol and hydrocyanic acid; it forms glistening prisms, m. p. 37°. It condenses with hydantoin to give 2 : 3 : 4-*trimethoxybenzylidenehydantoin*, $C_6H_2(OMe)_3CH{:}C<\begin{matrix}NH\cdot CO\\ |\\ CO-NH\end{matrix}$, pale yellow needles, m. p. 197°, which is reduced by sodium amalgam in water to 2 : 3 : 4-*trimethoxybenzylhydantoin*, thin, white needles, m. p. 154°. This is hydrolysed by boiling barium hydroxide to 2 : 3 : 4-*trimethoxyphenylalanine*, forming star-shaped aggregates of needles, m. p. 216°. If the hydrolysis is not carried to completion, α-*carbamido*-β-2 : 3 : 4-*trimethoxyphenylpropionic acid* is obtained, m. p. 189°. The trimethoxyphenylalanine is demethylated by boiling with hydriodic acid (*d* 1·70), giving 2 : 3 : 4-*trihydroxyphenylalanine*, crystallising in short, stout needles, m. p. 225° (decomp.). Its neutral solution reduces silver nitrate in the cold and gives a permanent blue colour with ferric chloride.

3 : 4 : 5-*Trihydroxyphenylalanine* was synthesised in a similar manner. It forms stout prisms, m. p. 290° (decomp.). In its low solubility it resembles 3 : 4-dihydroxyphenylalanine, but both the trihydroxyphenylalanines differ from this in not giving the characteristic reaction with the pigment-forming ferment, dopa-oxydase. 3 : 4 : 5-*Trimethoxybenzylidenehydantoin* forms yellow needles, decomp. 250—260°; 3 : 4 : 5-*trimethoxybenzylhydantoin*, long, white prisms, m. p. 172°; 3 : 4 : 5-*trimethoxyphenylalanine*, white needles, decomp. 220°. E. H. R.

Constitution of Phthalonic Acid. CORNILLOT (*Compt. rend.*, 1924, **178**, 713—715; cf. this vol., i, 294).—Phthalonic anhydride (1 mol.) is converted by phosphorus pentachloride (1 mol.), in presence of toluene, into α-*chlorophthalide*-α-*carboxylic chloride*, $CO<\begin{matrix}C_6H_4\\ |\\ O\end{matrix}>CCl\cdot COCl$, prisms, m. p. 70°, b. p. 120°/2 mm. The latter in moist air passes into the corresponding *acid*, white needles, m. p. 133°. The acid is stable in air; cold alkali slowly, and warm alkali very rapidly, affords phthalonic acid. The chloro-acid, or its chloride, is at once converted by alcohols into the corresponding esters. The *methyl* ester, stable, has m. p. 92°; the *ethyl* ester, m. p. 48°, b. p. 164°/5 mm., is gradually affected by moist air. The chloride, with aniline, affords the corresponding *anilide* (m. p. 137·5°), this being converted by concentrated alkali into phthalonanilic acid.

Phthalonic anhydride and methyl alcohol afford *methyl hydrogen phthalonate*, $C_6H_4(CO_2H)\cdot CO\cdot CO_2Me$, m. p. 94°; this ester separates from alcoholic solutions with 1 mol. of solvent of crystallisation

(removable in a vacuum), and is converted by phosphorus pentachloride into methyl α-chlorophthalide-α-carboxylate. E. E. T.

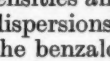
Isomerism of the Oximes. XVI. Action of Ultra-violet Light on Aldoximes and their Derivatives. O. L. BRADY and G. P. MCHUGH (*J. Chem. Soc.*, 1924, **125**, 547—554).—The action of ultra-violet light on nineteen aromatic aldoximes has been investigated. In nine cases, viz., *p*-methoxy- and 3 : 4-methylenedioxybenz*anti*aldoximes, benz*anti*aldoxime, *o*-, *m*-, and *p*-nitro-, and *o*-, *m*-, and *p*-chloro-benz*anti*aldoximes, conversion from the *anti*- to the *syn*-isomeride was accomplished, but in all these cases the *syn*-isomeride has been prepared by other means. It is evident, however, that the conversion is not dependent, as Ciusa supposed (A., 1907, i, 137), on the presence of a negative substituent in the benzene ring. Eight cases were examined in which the *syn*-isomeride had not been prepared by other means: *o*-methoxy-, 5-bromo-*o*-methoxy-, 2 : 4-dinitro-, 3-nitro-*p*-dimethylamino-, 6-nitro-3 : 4-methylenedioxy-, 5-nitro-3 : 4-dimethoxy-, 6-nitro-3 : 4-dimethoxy-, and 5-bromo-4-hydroxy-3-methoxy-benz*anti*aldoximes, and in no case did conversion take place under the influence of ultra-violet light. With 3 : 4-dimethoxybenz*anti*aldoxime no isomeric change occurred, although the *syn*-compound has been obtained by special means. 5-Bromo-3 : 4-dimethoxybenz*anti*aldoxime suffered demethylation when exposed to ultra-violet light, giving 5-bromo-4-hydroxy-3-methoxybenz*anti*aldoxime.

A number of derivatives of the *anti*-oximes have been examined, and of these the three *O*-ethers, viz., the methyl ethers of *m*- and *p*-nitrobenz*anti*aldoximes and the benzyl ether of *p*-nitrobenz*anti*aldoxime, were converted into the *syn*-isomeride, although not so completely as the oximes. Of the two nitrogen ethers investigated, the *N*-methyl ether of benzaldoxime is decomposed, yielding benzonitrile, whilst the *N*-methyl ether of *m*-nitrobenzaldoxime undergoes no change. R. B.

Configuration of Stereoisomeric Oximes and the Structure of Oxime-*N*-ethers and *aci*-Nitro Derivatives. K. VON AUWERS and B. OTTENS (*Ber.*, 1924, **57**, [*B*], 446—461).—The spectrochemical behaviour of a series of oximes is found to be closely similar to that of their *O*-alkyl and acyl derivatives. Since the latter substances necessarily contain the group :C:N·OR, it follows that the oximes themselves must have the constitution :C:N·OH. Confirmation of this view is found in the observation that the benzylideneamines, which undoubtedly contain the similar, conjugated group, ·C:C·CH:N–, have molecular exaltations which are of the same order of magnitude as those of the oximes. A consideration of the magnitudes of the physical constants of the oximes renders it very improbable that a three-membered ring, $>C<\overset{N-}{\underset{O}{|}}$, is present, although a direct estimation of the influence of the ring is impossible, since there is no known compound in which its presence has been established definitely. It is, however, scarcely conceivable that

such a ring, even when conjugated with a double linking, could produce the observed remarkable increase in index of refraction and dispersive power, particularly since heterocyclic rings containing nitrogen, such as and , are optically indifferent. The "nitrone" formula, :C:NH:O, for the oximes is excluded, since their *N*-ethers are characterised by unusually high dispersive power, which could scarcely fall to a small fraction in the oximes themselves if the latter substances yielded the *N*-ethers simply by the replacement of hydrogen by alkyl without any structural change.

Attempts to discriminate between the *cis*- and *trans*-forms of stereoisomeric oximes, on the hypothesis that the former varieties exhibit higher densities and refractive indices but smaller molecular refractions and dispersions than the *trans*-compounds, are described. In the cases of the benzaldoximes and their ethers, it is found that the α-oxime has the *syn*-configuration; this is opposed to the customary view, but is in harmony with the recent observations of Meisenheimer (A., 1922, i, 152) and Beckmann (A., 1923, i, 228). In a number of other instances, the interpretation of the observed results is much more difficult; at present, it is not possible to form a definite opinion as to the value of spectrochemical evidence in this field.

The optical behaviour of the *N*-ethers of oximes is strongly against the existence of a three-membered ring,  , the presence of which could not explain the observed powerful exaltations; it is consonant with the structure :C:NR:O, experimental evidence for which has been adduced by Semper and Lichtenstadt (A., 1918, i, 437) and by Staudinger (A., 1919, i, 584).

The optical properties of the carbamidoximes (cf. Conduché, A., 1908, i, 12, 154), of the *aci*-forms of the nitroparaffins and of tetranitromethane are in agreement with the constitutions, $RR'C{:}N(:O)\cdot CO\cdot NH_2$, $RR'C{:}N(:O)\cdot OH$, and $(NO_2)_2C{:}N(:O)\cdot O\cdot NO_2$, respectively.

The physical constants have been observed partly with homogeneous material, partly with substances dissolved in quinoline which is found to be a very suitable solvent for this purpose. The following data, amongst others, are recorded. Heptaldoxime, $d_4^{99\cdot8}$ 0·8219, $n_{He}^{99\cdot8}$ 1·41514. α-Mesityl oxideoxime, b. p. 84°/11 mm., d_4^{100} 0·876, n_{He}^{100} 1·450. β-Mesityl oxideoxime, b. p. 95°/11 mm., d_4^{100} 0·881, n_{He}^{100} 1·462. α-Mesityl oxideoxime acetate, b. p. 101°/11 mm., d_4^{20} 0·986, n_{He}^{20} 1·474. β-Mesityl oxideoxime acetate, b. p. 107°/14 mm., d_4^{20} 0·990, n_{He}^{20} 1·478. α-Mesityl oxideoxime benzyl ether, b. p. 131°/11 mm., d_4^{20} 0·987, n_{He}^{20} 1·533. α-Benzaldoxime, m. p. 35°, d_4^{20} 1·110, n_{He}^{20} 1·593. α-Benzaldoxime *O*-methyl ether, b. p. 79°/11 mm., d_4^{20} 1·020, n_{He}^{20} 1·548. β-*Benzaldoxime* O-*methyl ether*, b. p. 79°/11 mm., d_4^{20} 1·028, n_{He}^{20} 1·550. α-Benzaldoxime acetate, d_4^{20} 1·107, n_{He}^{20} 1·544.

Heptaldoxime *N*-benzyl ether, $d_4^{99\cdot6}$ 0·9293, $n_{He}^{99\cdot6}$ 1·49714. Furfur-

aldoxime *N*-methyl ether, $d_4^{59\cdot8}$ 1·1185, $n_{He}^{99\cdot8}$ 1·56351. Furfuraldoxime *N*-benzyl ether, $d_4^{99\cdot7}$ 1·1270, $n_{He}^{99\cdot7}$ 1·59871. β-Benzaldoxime *N*-methyl ether, $d_4^{99\cdot9}$ 1·0528, $n_{He}^{99\cdot9}$ 1·59189. o-*Chlorobenzaldoxime* N-*phenyl ether*, coarse, pale yellow crystals, m. p. 81·5—82·5° (from *o*-chlorobenzaldehyde and phenylhydroxylamine), $d_4^{100\cdot3}$ 1·2008, $n_{He}^{100\cdot3}$ 1·64853. Phenylnitromethane, $d_4^{24\cdot7}$ 1·1540, $n_{He}^{24\cdot7}$ 1·52850. aci-*Phenylnitromethane methyl ether*, from nitromethane, methyl sulphate, and sodium hydroxide, a pale yellow liquid with an odour of bitter almonds, b. p. 117°/15 mm., ca. 83°/1·5 mm., $d_4^{15\cdot0}$ 1·1241, $n_{He}^{15\cdot0}$ 1·58708. Tetranitromethane, $d_4^{16\cdot9}$ 1·6425, $n_{He}^{16\cdot9}$ 1·43976.

Benzylidenemethylamine, CHPh:NMe, b. p. 185°, d_4^{20} 0·962, n_{He}^{20} 1·553. Benzylidene-ethylamine, b. p. 195°, d_4^{20} 0·937, n_{He}^{20} 1·541. Benzylidene*iso*amylamine, b. p. 245°, d_4^{20} 0·906, n_{He}^{20} 1·519. Benzylideneaniline, b. p. 300°, $d_4^{99\cdot3}$ 1·0041, $n_{He}^{99\cdot3}$ 1·61041. Benzylidene-*o*-toluidine, b. p. 314°, d_4^{20} 1·041, n_{He}^{20} 1·635. H. W.

Reactions of Cinnamalphenylnitrone. D. Bigiavi and M. Marri (*Gazzetta*, 1924, **54**, 99—113).—Among the products obtained by Weitnauer (Dissertation, Basle, 1904) on reducing phenyl*iso*cinnamaldoxime by means of sodium or sodium amalgam and absolute alcohol were two compounds described by this author as (1) liquid secondary base, b. p. 190—190·5°/8 mm., and (2) solid secondary base, m. p. 90—90·5°, and regarded as having the structures, $NHPh\cdot CH_2\cdot CH_2\cdot CH_2Ph$, and $NHPh\cdot CH(OH)\cdot CH_2\cdot CH_2Ph$, respectively. The authors show that the solid base, m. p. 90°, is actually hydrocinnamanilide, its formation being the result of migration of the oxygen atom of the phenyl*iso*cinnamaldoxime from the nitrogen to the adjacent carbon atom, followed by hydrogenation of the cinnamanilide thus formed: $O:NPh:CH\cdot CH:CHPh \longrightarrow NHPh\cdot CO\cdot CH:CHPh \longrightarrow NHPh\cdot CO\cdot CH_2\cdot CH_2Ph$. Similar transpositions are exhibited by a large number of compounds, including nitrones (cf. Miescher, "Nitrone und Nitrene," Zurich, 1918, 20). By acetic anhydride, cinnamalphenylnitrone is converted quantitatively into the acetyl derivative of cinnamanilide as the result of an intensely exothermic reaction, hydrolysis then yielding the anilide: $O:NPh:CH\cdot CH:CHPh \longrightarrow NHPh\cdot CO\cdot CH:CHPh$; catalytic reduction of cinnamanilide by means of hydrogen and platinum black yields hydrocinnamanilide, identical with the product obtained by heating aniline with hydrocinnamic acid.

By catalytic reduction, Cusmano (A., 1922, i, 143) has converted nitrones into hydroxylamines. From cinnamalphenylnitrone this author has obtained, by reduction with hydrogen and platinum black, a compound which is apparently a hydroxylamine. This marked divergence in behaviour must be due to the presence of conjugated double bonds in the molecule of cinnamalphenylnitrone.

By dilute sulphuric acid, cinnamalphenylnitrone is readily converted into the Schiff's base of *p*-aminophenol:

$$O:NPh:CH\cdot CH:CHPh \longrightarrow OH\cdot C_6H_4\cdot N:CH\cdot CH:CHPh$$

(cf. Angeli, Alessandri, and Pegna, A., 1910, i, 552). Analogous reactions produced by dilute sulphuric acid are: $O:NH_2Ph \longrightarrow OH\cdot C_6H_4\cdot NH_2$; $O:NPh:NPh \longrightarrow OH\cdot C_6H_4\cdot N:NPh$; $O:NPhMe_2$

$\longrightarrow$ $OH{\cdot}C_6H_4{\cdot}NMe_2$. On other nitrones, the acid exerts a hydrolysing action, the original aldehyde or ketone and aryhydroxylamine being regenerated.

The *acetyl* derivative of cinnamanilide, $C_{17}H_{15}O_2N$, forms acicular crystals, m. p. 138—139°.

Hydrocinnamanilide, $C_{15}H_{15}ON$, crystallises in lustrous, white needles, m. p. 98°, and exhibits the normal molecular weight in acetic acid. It is stable towards alcoholic potassium hydroxide, but is rapidly hydrolysed when heated with dilute sulphuric acid. Sodium and alcohol reduce it to aniline and another base, which is probably Weitnauer's liquid secondary base. With nitrous acid, it appears to yield a nitrosoamine. Its *acetyl* derivative, $C_{17}H_{17}O_2N$, forms minute, refractive crystals, m. p. 45°. T. H. P.

Oxides of the Stereoisomeric Trithiobenzaldehydes. O. Hinsberg (*Ber.*, 1924, **57**, [*B*], 417—419).—A detailed reply to the criticisms of Fromm and Schultis (A., 1923, i, 580) on the author's work (A., 1914, i, 185). Contrary to the views of Fromm and Schultis, α-trithiobenzaldehyde pentoxide (disulphone-sulphoxide) must be regarded as a homogeneous substance. The individuality of δ-trithiobenzaldehyde tetroxide is not, however, established with equal certainty, and it is possible that the product is a difficultly separable mixture of the tri-, tetra-, and pent-oxides, but this is not conclusively proved by the experiments of Fromm and Schultis. Valid evidence against the existence of δ-trithiobenzaldehyde has not been adduced. H. W.

Pinacolin Transformation in the Dehydration of 1 : 2-Dimethyl*cyclo*hexane-1 : 2-diol. S. Nametkin and N. Delektorsky (*Ber.*, 1924, **57**, [*B*], 583—587).—1 : 2-Dimethyl*cyclo*hexane-1 : 2-diol, m. p. 92—93°, prepared by hydrating the corresponding oxide at the ordinary temperature with very dilute sulphuric acid, was heated at 150—160° for 3 hours with acidulated water. On cooling, the pinacolin separated as an oil possessing a peppermint-like odour and distilling, after purification by means of its semicarbazone, at 60·5°/20 mm. It was found to be identical with 1-methyl-1-*cyclo*pentyl methyl ketone (Meerwein, A., 1919, i, 162). The pinacolin transformation is therefore accompanied by the change from a six-ring to a five-ring. The reverse change occurs on dehydrating 1-methyl-1-α-hydroxyethyl*cyclo*pentane, the product being 1 : 2-dimethyl-Δ^1-*cyclo*hexene (Meerwein, *loc. cit.*). F. A. M.

Oxidation of Sabinene with Chromyl Chloride. A Correction. G. G. Henderson and J. M. Robertson (*J. Chem. Soc.*, 1924, **125**, 765—766).—The supposed 4-*iso*propylidene-*cyclo*hexanone obtained by the oxidation of sabinene with chromyl chloride (*Chem. Soc. Trans.*, 1922, **121**, 2717) has now been found to be *p*-tolyl methyl ketone. The alcohol obtained by its reduction is therefore *p*-tolylmethylcarbinol. The formation of this ketone from sabinene is attributed to oxidation of part of the sabinene to cymene, which with chromyl chloride forms the compound $C_{10}H_{14},2CrO_2Cl_2$, from which *p*-tolyl methyl ketone is formed on decomposition with water. R. B.

Change of State of Aggregation and Polymorphism. III. Polymorphism of Benzophenone. K. SCHAUM and K. UNGER (*Z. anorg. Chem.*, 1924, **132**, 90—98; cf. A., 1916, i, 405).—The instability of the metastable form of benzophenone makes the investigation of its pseudo-binary character difficult. On this account, the *p*-halogen and *p*-hydroxy derivatives were examined. These were found to be monotropic trimorphic, but the m. p. of the three forms lie very close together, not more than 0·5° apart. The effect of previous history on the m. p. of benzophenone was examined. No difference could be detected after heating for different periods of time at different temperatures. H. T.

Preparation of 3 : 3′-Dinitrobenzophenone. E. DE B. BARNETT and M. A. MATTHEWS (*J. Chem. Soc.*, 1924, **125**, 767).—By nitration of benzophenone in sulphuric acid solution with nitric acid (*d* 1·50) at 25—30°, a yield of 50% of theory of crude 3 : 3′-dinitrobenzophenone was obtained, which after one crystallisation from methyl ethyl ketone melted at 155°. R. B.

Valency. I. Estimation of the Strength of the Bond between a Radical and Carbon. A. SCHONBERG, R. ABELSDORFF, H. KIRCHRATH, W. MALCHOW, and A. ROSENBACH (*Annalen*, 1924, **436**, 205—218).—The reaction between benzophenone and sodamide, first studied by Haller (A., 1908, i, 987), has been applied to substituted aromatic ketones. Benzophenone, in toluene solution, gives as a final product benzamide: $Ph_2CO+NaNH_2 \longrightarrow Ph_2C(NH_2)ONa \longrightarrow C_6H_6+Ph\cdot CO\cdot NHNa \longrightarrow Ph\cdot CO\cdot NH_2$. With an unsymmetrical substituted benzophenone, the reaction may proceed in two ways, giving benzene and a substituted benzamide, or a substituted benzene and benzamide. It is shown that Haller's explanation (*loc. cit.*) of the reaction is incorrect; for instance, diphenyl phenyl ketone with sodamide in toluene solution gives diphenyl, which agrees with the above scheme. The yields in this reaction are practically quantitative, so that by determining the proportions of the free acids (obtained by hydrolysis of the amides) formed, it is possible to determine the relative affinity of the various radicals for carbonyl carbon, and comparative numerical values can be assigned to each radical. Taking the affinity of the phenyl radical as the unit, the following values are assigned to substituted phenyl radicals containing the substituent groups indicated:—*m*-chloro-, 0·05—0·32; *m*-bromo-, 0·08—0·38; *p*-chloro-, 0·18—0·51; *p*-bromo-, 0·18—0·65; *p*-methoxy-, 1·12—2·16; and *p*-dimethylamino-, about 1·23. The value for the radicals CPh_3^- and $CPh_2(ONa)^-$ is less than 0·14. If the ketone is not decomposed by sodamide, for example, phenyl triphenylmethyl ketone, hydrolysis with alkali is resorted to, the final products being triphenylacetic acid and benzoic acid, in proportions depending on the relative affinities of the triphenylmethyl and phenyl radicals. The method fails with aliphatic ketones, a sodium compound of the ketone being formed.

p-*Methylmercaptobenzophenone*, colourless prisms, m. p. 79°, was synthesised from benzoyl chloride, methyl phenyl sulphide, and

aluminium chloride in carbon disulphide solution; (*phenylhydrazone*, colourless crystals, m. p. 90°). p-*Methylmercaptobenzoic acid*, by the action of sodamide on the ketone in toluene solution, forms prisms, m. p. 192°. 4 : 4′-Dimethylmercaptobenzophenone, from thioanisole and oxalyl chloride in presence of aluminium chloride in ice-cold carbon disulphide solution, forms colourless scales, m. p. 125·5° (anil, yellow prisms, m. p. 135°). A. E. C.

Isomeric *p′*-Methylchalkones [*p*-Tolyl Styryl Ketones]. C. WEYGAND (*Ber.*, 1924, **57**, [*B*], 413—417).—*p*-Tolyl methyl ketone, condensed with benzaldehyde and sodium ethoxide, yields *p*-methylchalkone (*p*-tolyl styryl ketone), m. p. 590 (cf. Sorge, A., 1902, i, 379); on recrystallising several months later, it was suddenly converted into the isomeric form, m. p. 77°, described by Kostanecki (A., 1896, i, 688), and during the night all the other uncovered preparations were converted into the same modification. All subsequent preparations gave only the 77° form, which on heating to 135° and cooling deposits the form, m. p. 59°; this is at once changed into the 77° modification when touched with a crystal of the latter. Both forms could be crystallised from suitable solvents at first, but once the 77° form had appeared it became nearly impossible to recover the 59° form from solution except by working at low temperatures or in air-tight vessels. Both forms give orange-yellow solutions in concentrated sulphuric acid, the 77° form being deposited on dilution; both yield the same *dibromide* as a white, crystalline powder, m. p. 175—176°, the same *compound* with stannic chloride, m. p. 85° (not sharp), and the same aniline additive *compound*, m. p. 141°. At 21°, 100 g. of benzene dissolve about 55·8 g. of the 77° form, and 166·8 g. of the 59° form. Both forms have normal molecular weights in benzene. F. A. M.

Insecticides. IV. Constitution of Tetrahydropyrethrone. H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, **7**, 236—244).—It was shown in a previous paper (p. 523) that reduction of pyrethrolone by the Paal–Skita method gives tetrahydropyrethrolone. When the reduction is pushed to the limit, the hydroxyl group is also reduced, tetrahydropyrethrone being formed. Complete reduction is effected more readily with the acetate or the methyl ether than with pyrethrolone itself. *Tetrahydropyrethrone* is a colourless, mobile liquid with a faint, ethereal odour, b. p. 100—101°/12 mm. Its constitution, determined from its oxidation products, is 3-*methyl*-2-n-*amyl*cyclo*pentanone*,

$$\begin{matrix} CH_2\cdot CHMe \\ | \\ CH_2 \text{---} CO \end{matrix} > CH\cdot C_5H_{11}.$$

The *semicarbazone* varies in melting point from 160° to 194°, according to the manner in which the ketone is prepared. That of m. p. 194°, from the ketone obtained by reduction of pyrethrolone acetate, is the *lævo* form; that having m. p. 160° is the *racemic* form. The p-*nitrophenylhydrazone* (*r*-form) forms yellow needles, m. p. 87°. By oxidation of tetrahydropyrethrone with potassium permanganate, hexoic and lævulic acids were obtained. Their

formation is compatible with two possible formulæ, a *cyclo*pentane derivative with the keto group in the ring or a *cyclo*butane derivative with the keto group in the side chain. The oxime of the former should give a lactam by the Beckmann change, whilst the oxime of the latter should give an acid amide. The *oxime* of tetrahydropyrethrone is a colourless oil, b. p. 84—85°/0·1 mm., which, by treatment with concentrated sulphuric acid, is converted into the iso-*oxime*, a viscous oil, b. p. 120°/0·1 mm. The latter is converted by boiling hydrochloric acid into *δ-amino-γ-methyldecoic acid*, which by treatment with nitrous acid is converted into the *lactone* of *δ-hydroxy-γ-methyldecoic acid*. The constitution of tetrahydropyrethrone as 3-methyl-2-*n*-amyl*cyclo*pentanone is therefore established. E. H. R.

Insecticides. V. Synthesis of Tetrahydropyrethrone, the Reduction Product of Pyrethrolone. H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, **7**, 245—259).—The constitution of tetrahydropyrethrone, which was concluded to be 3-methyl-2-*n*-amyl*cyclo*pentanone (preceding abstract), has been confirmed by synthesis as follows: *Ethyl α-bromoheptoate* (colourless oil, b. p. 106—107°/12 mm.) was condensed with ethyl lævulate, forming the *γ-lactone* of *ethyl hydrogen γ-hydroxy-γ-methylnonane-αδ-dicarboxylate*, $C_5H_{11}\cdot CH(CO_2Et)\cdot CMe\cdot[CH_2]_2\cdot CO$ (lactone ring O), a colourless, viscous oil, b. p. 130°/0·1 mm. When hydrolysed with 25% potassium hydroxide, the lactone ester is decomposed to a great extent into heptoic and lævulic acids, and only a small yield of *γ-hydroxy-β-methylnonane-αδ-dicarboxylic acid lactone* is obtained, white crystals, m. p. 86—87°. When the disodium salt of the free adipic acid is heated, it loses water and carbon dioxide, forming *γ-methyl-Δγ-decenoic acid*, $C_5H_{11}\cdot CH{:}CMe\cdot[CH_2]_2\cdot CO_2H$, a viscous oil of peculiar odour, b. p. 160—163°/15 mm. (*p-toluidide*, m. p. 44—45°; *α-naphthylamide*, m. p. 63—64°), which is reduced by the Paal–Skita method to *γ-methyldecoic acid*, a colourless oil, b. p. 150—152°/12 mm. (*p-toluidide*, m. p. 34—36°; *α-naphthylamide*, m. p. 61—62°).

When the condensation of ethyl α-bromoheptoate and ethyl lævulate with zinc was continued for a prolonged period at 150°, one of the reaction products was a butylene derivative, *ethyl hydrogen γ-methyl-Δγ-nonylene-αδ-dicarboxylate* (*δ-carbethoxy-γ-methyl-Δγ-decenoic acid*), $C_5H_{11}\cdot C(CO_2Et){:}CMe\cdot[CH_2]_2\cdot CO_2H$, a colourless oil, b. p. 150°/0·4 mm., which could not be reduced with hydrogen (Paal–Skita) or sodium amalgam; the *ethyl* ester has b. p 170—180°/15 mm. When the ester was boiled with sodium and xylene, and the sodium compound of the resulting methylamyl*cyclo*pentanonecarboxylate boiled with 20% sulphuric acid, *3-methyl-2-amyl-Δ²-cyclopentenone* was obtained, a colourless oil, b. p. 115—117°/12 mm. (*semicarbazone*, m. p. 175—176°; *p-nitrophenylhydrazone*, m. p. 118—119°). The unsaturated ketone could only be reduced by passing its vapour with hydrogen over nickel at 240—250°. The resulting 3-methyl-2-amyl*cyclo*pentanone was identical with tetrahydropyrethrone.

The following compounds were obtained in unsuccessful attempts to effect the synthesis: 3-*Methyl*-5-n-*amyl*cyclo*pentanone*, colourless liquid, b. p. 107—109°/14 mm. (*semicarbazone*, m. p. 147—148°; p-*nitrophenylhydrazone*, m. p. 134—135°), by condensing ethyl β-methyladipate to a *cyclo*pentanonecarboxylic acid by Dieckmann's method (A., 1900, i, 297) and heating the sodium salt of this acid with amyl bromide. *Ethyl* β-*methylbutane*-ααδ-*tricarboxylate*, colourless oil, b. p. 135°/0·4 mm. (from ethyl malonate and ethyl γ-bromovalerate, in presence of sodium), reacted slowly with *n*-amyl bromide in presence of alcoholic sodium ethoxide, giving the same methylamyl*cyclo*pentanone as above and by-products.

E. H. R.

Insecticides. III. Constitution of Pyrethrolone. H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, **7**, 212—235).—The alcoholic constituent of the active substances in insect powder, pyrethrolone, $C_{11}H_{16}O_2$, is obtained from the semicarbazone already described by careful cold hydrolysis with potassium hydrogen sulphate in presence of benzene and water. It forms a viscous oil, b. p. 111—112°/0·05 mm., $[\alpha]_D^{20}$ −6·2° (approx.). Pyrethrolone probably has the constitution 1-*methyl*-2-*pentadienyl*-cyclo*pentane*-4-*ol*-3-*one*, $\begin{matrix} CH_2\cdot CHMe \\ | \\ OH\cdot CH \end{matrix}\!\!>\!\!\begin{matrix} \\ \\ CO \end{matrix}\!\!>CH\cdot CH_2\cdot CH{:}C{:}CHMe$; it forms a p-*nitrophenylosazone*, a brown, microcrystalline powder, decomposing above 350°; and an *acetate*, $C_{13}H_{18}O_3$, a colourless, mobile oil, b. p. 104—105°/0·5 mm., $[\alpha]_D^{15}$ −23·79°, which forms a crystalline *semicarbazone*, m. p. 143—145°. When treated with alkali it undergoes autoxidation, forming *dehydropyrethrolone*, a mobile oil, b. p. 82°/0·05 mm., which gives a *semicarbazone*, m. p. 251°, and a second oxidation product, a viscous oil, probably a polymerised form of the first; both are weakly acidic. By methylation with methyl alcohol and concentrated sulphuric acid, pyrethrolone semicarbazone forms a *methyl* ether, m. p. 183°, which, by removal of the semicarbazone group gives the *methyl* ether of pyrethrolone, a mobile oil, b. p. 82—83°/0·25 mm. Pyrethrolone itself can be methylated with methyl sulphate to give the same product, but with methyl alcohol and sulphuric acid it gives a different product forming a *semicarbazone*, m. p. 207°. The *ethyl* ether of pyrethrolone is a colourless liquid, b. p. 102—103° in the highest vacuum; *semicarbazone*, m. p. 179—180°.

When pyrethrolone is reduced by the Paal–Skita method, it takes up 2 mols. of hydrogen, forming *tetrahydropyrethrolone*, which is shown (p. 521) to be 1-*methyl*-2-n-*amyl*cyclo*pentane*-4-*ol*-3-*one*; it is a viscous oil, b. p. 160—162°/10 mm., 108—110°/0·1 mm.; $[\alpha]_D^{20}$ −11·32°, with strong reducing properties. When esterified with chrysanthemumyl chloride, it gives a product having no insecticidal properties. Tetrahydropyrethrolone forms a p-*nitrophenylosazone*, decomposing above 350°; a *semicarbazone*, m. p. 189—190° (decomp.); an *acetate*, a mobile oil, b. p. 110°/0·16 mm., and a *methyl* ether, a colourless, mobile oil, b. p. 128°/12 mm., obtained by reduction of pyrethrolone methyl ether. By oxid-

ation with potassium permanganate, tetrahydropyrethrolone gives hexoic acid. Decomposition of the mono-ozonide of pyrethrolone gives acetaldehyde and acetic acid, showing the presence of an ethylidene group. Malonic acid was also obtained by further oxidising the products obtained from the ozonide with hydrogen peroxide. By ozonisation of pyrethrolone acetate, an acid was obtained which appeared to be an *acetoxymethylcyclopentenone-homocarboxylic acid*, $\begin{matrix}CH-CHMe\\ \|\quad\quad\\ C(OAc)\cdot CO\end{matrix}>CH\cdot CH_2\cdot CO_2H$; m. p. 136—138°.

The above observations, together with the fact that pyrethrolone only absorbs 1 mol. of bromine with ease, support the view that the side chain contains the allene grouping, although this grouping has not previously been found in a natural product. E. H. R.

Hydroxyhydrindone and Chromanone. F. Mayer and L. van Zütphen (*Ber.*, 1924, **57**, [*B*], 618).—A correction. In a previous paper (this vol., i, 410) the authors claimed to have synthesised chromanone by the action of aluminium chloride on *o*-hydroxyphenyl β-chloroethyl ketone. The product is now admitted to be 7-hydroxyhydrindone, b. p. 128°/13 mm. The benzylidene compound is coloured yellow by sodium hydroxide solution, but is not dissolved even on boiling. (Cf. Krollpfeiffer and Schultze, following abstract.) F. A. M.

Formation of Hydroxyhydrindones from Phenyl Esters of β-Halogenpropionic Acids by Heating with Aluminium Chloride. F. Krollpfeiffer and H. Schultze (*Ber.*, 1924, **57**, [*B*], 600—601; cf. this vol., i, 411).—*p-Tolyl β-bromopropionate* is obtained in quantitative yield by heating *p*-cresol with β-propionyl chloride and is a colourless oil, b. p. 162°/14 mm. When it is heated with twice its weight of aluminium chloride at 100—120°, and the product decomposed with iced hydrochloric acid, 80% of the theoretical yield of *1-hydroxy-4-tolyl β-bromoethyl ketone* is obtained, forming small, colourless plates, m. p. 72—73°. At 160—170° the product is 4-methyl-7-hydroxyhydrindone, m. p. 110—111°, the yield being 60% of theory. This provides strong evidence that the "γ-chromanone" obtained by Mayer and van Zütphen (this vol., i, 410) is really 7-hydroxyhydrindone. (Cf. Mayer and Zütphen, preceding abstract.) F. A. M.

Synthesis of *m*-Dimethoxyphenyl Ethyl and Methyl Ketones. F. Mauthner (*J. pr. Chem.*, 1924, [ii], **107**, 103—108).—To obtain better yields of 3 : 5-dimethoxyphenyl ethyl ketone than were obtained from 3 : 5-dimethoxybenzoyl chloride and zinc ethyl iodide (A., 1922, i, 457), methyl 3 : 5-dimethoxybenzoate was condensed with ethyl acetate by the Claisen method and the *ethyl 3 : 5-dimethoxybenzoylacetate*, a pale yellow oil (*pyrazolone* derivative with phenylhydrazine, m. p. 153—154°), was converted by treatment with methyl iodide and sodium ethoxide, followed by hydrolysis with 25% sulphuric acid, into 3 : 5-dimethoxyphenyl ethyl ketone, colourless needles, m. p. 34—35° (*semicarbazone*, colourless needles, m. p. 130—131°). Hydrolysis of ethyl 3 : 5-di-

methoxybenzoylacetate with 25% sulphuric acid yields 3 : 5-*dimethoxyphenyl methyl ketone*, colourless needles, m. p. 42—43°, b. p. 151—152°/10 mm. (p-*nitrophenylhydrazone*, reddish-yellow needles, m. p. 157—158°; *semicarbazone*, colourless needles, m. p. 186—187°). Condensation of 3 : 5-dimethoxybenzaldehyde and sodium propionate by the Perkin reaction gives 3 : 5-*dimethoxy-α-methylcinnamic acid*, colourless needles, m. p. 153—154°, but attempts to convert this into 3 : 5-dimethoxypropenylbenzene through loss of carbon dioxide failed. 3 : 5-*Dimethoxyphenylethylcarbinol*, b. p. 170—171°/12 mm. (*phenylurethane*, colourless plates, m. p. 86—87°), was obtained by the Grignard reaction from 3 : 5-dimethoxybenzaldehyde and ethyl iodide; with excess of Grignard reagent 3 : 5-*dimethoxypropenylbenzene* was formed but rapidly polymerised. R. B.

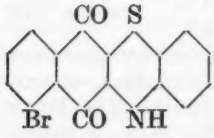
Quinones of Linear Ring Systems with Reactive Halogen in the Non-quinonoid Nucleus. K. FRIES and E. KÖHLER (*Ber.*, 1924, **57**, [*B*], 496—510).—A continuation of previous work (Fries and Kerkow, A., 1922, i, 577). 5-Bromoacetnaphthalide can be prepared by the reduction of 5-bromo-1-nitronaphthalene with iron filings and acetic acid or with zinc dust and ammonium chloride and subsequent acetylation of the product or, more economically, by means of iron powder and glacial acetic acid and subsequent treatment of the solution with acetic anhydride. It is converted by a mixture of glacial acetic acid and nitric acid (*d* 1·48) at −2° into a mixture of 5-bromo-2-nitroacetonaphthalide and 5-bromo-4-nitroacetonaphthalide (m. p. 225°), which can be only incompletely separated by fractional crystallisation. Treatment of the mixture with aqueous-alcoholic sodium hydroxide solution leads to the ready isolation of 5-*bromo*-4-*nitro*-α-*naphthylamine*, reddish-brown needles or prismatic crystals, m. p. 192° (*monoacetate*, pale yellow, lustrous needles, m. p. 225°; *diacetate*, pale brown leaflets, m. p. 170°), and 5-*bromo*-2-*nitroacetonaphthalide*, m. p. 240°. 5-Bromo-4-nitro-α-naphthylamine is reduced by stannous chloride and hydrochloric acid in glacial acetic acid solution to 5-*bromo*-1 : 4-*naphthylenediamine*, slender, pale green needles, m. p. 132° (*dihydrochloride*, slender, colourless needles; *diacetyl* compound, colourless needles, m. p. 257°). 5-*Bromo*-1 : 4-*naphthaquinone*, golden-yellow prisms, m. p. 160°, and 5-*bromo*-2-*anilino*-1 : 4-*naphthaquinone*, red, prismatic leaflets, m. p. 219°, are described. The diamine hydrochloride (or the stannic double salt) is transformed by exhaustive chlorination in the presence of glacial acetic and concentrated hydrochloric acids into 2 : 2 : 3 : 3-*tetrachloro*-5-*bromo*-1 : 4-*diketo*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, $C_6H_3Br<\begin{matrix}CO\cdot CCl_2\\ CO\cdot CCl_2\end{matrix}$, needles or monoclinic crystals, m. p. 120°, which is reduced by stannous chloride to 2 : 3-*dichloro*-5-*bromo*-1 : 4-*dihydroxynaphthalene*, colourless needles, m. p. 196° (*acetate*, needles, m. p. 154°). The latter substance is oxidised by ferric chloride to 2 : 3-*dichloro*-5-*bromo*-1 : 4-*naphthaquinone*, pale yellow, prismatic crystals, m. p. 180°, which, with aniline, gives 3-*chloro*-5-*bromo*-2-*anilino*-1 : 4-*naphtha*-

quinone, dark red needles, m. p. 239° (the assumption that the chlorine atom in position 2 suffers replacement is arbitrary).

[With G. SCHÜRMANN.]—A similar sequence of changes starting from 8-chloro-4-nitro-α-acetnaphthalide (which is the main product of the nitration of 8-chloro-α-acetnaphthalide) leads to the production of 5-chloro-1 : 4-naphthaquinone and its derivatives. The following compounds are described: 8-*Chloro*-4-*nitro*-α-*naphthylamine*, brownish-red, lustrous plates, m. p. 203° (*acetyl* derivative, needles, m. p. 167°); 5-*chloro*-1 : 4-*naphthylenediamine*, slender, pale yellow needles, m. p. about 116° (decomp.) (*diacetyl* derivative, slender, colourless needles, m. p. 269°); 5-*chloro*-1 : 4-*naphthaquinone*, yellow needles, m. p. 163°; 5-*chloro*-2-*anilino*-1 : 4-*naphthaquinone*, red needles with a bronzy lustre, m. p. 219°; 2 : 2 : 3 : 3 : 5-*pentachloro*-1 : 4-*dihydroxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, colourless leaflets, m. p. (indefinite) 82°; 2 : 3 : 5-*trichloro*-1 : 4-*dihydroxynaphthalene*, colourless needles, m. p. 204° (*acetate*, needles, m. p. 162°); 2 : 3 : 5-*trichloro*-1 : 4-*naphthaquinone*, coarse yellow needles, m. p. 156°; 3 : 5-*dichloro*-2-*anilino*-1 : 4-*naphthaquinone*, dark red needles, m. p. 225°; 3-*chloro*-2 : 5-*dianilino*-1 : 4-*naphthaquinone*, needles, m. p. 221°.

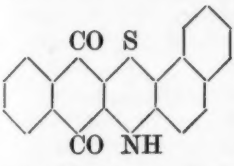
5-*Bromo*-2-*nitro*-α-*naphthylamine*, orange-red needles, m. p. 223°, is obtained by hydrolysing the corresponding monoacetyl derivative (see above) with sulphuric acid (*diacetyl* derivative, m. p. 133°). The acetyl compound is converted by boiling, 2*N*-sodium hydroxide solution into 5-*bromo*-2-*nitro*-α-*naphthol*, golden-yellow leaflets, m. p. 142°. 5-*Bromo*-1 : 2-*naphthylenediamine*, colourless plates or slender needles, m. p. 122°, is obtained by reduction of the nitro-amine with tin and hydrochloric acid; the corresponding *diacetyl* derivative, prismatic crystals, m. p. 287°, is transformed by boiling alcoholic sodium hydroxide solution into 6-bromo-2-methyl-αβ-naphthiminazole, colourless, slender needles, m. p. 242°, which is also obtained by the reduction of 5-bromo-2-nitro-α-naphthylamine with stannous chloride in glacial acetic acid solution. The diamine condenses with benzil in alcoholic solution to form the *quinoxaline* derivative, $C_{24}H_{15}N_2Br$, pale yellow needles, m. p. 214°. 3 : 5-*Dichloro*-5-*bromo*-1 : 2-*diketo*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (obtained by chlorination of the diamine), apparently monoclinic crystals, m. p. 93°, 3-*chloro*-5-*bromo*-1 : 2-*dihydroxynaphthalene*, colourless needles, m. p. 176° (*diacetyl* derivative, coarse crystals, m. p. 147°), and 3-*chloro*-5-*bromo*-1 : 2-*naphthaquinone*, small, red plates, m. p. 177°, are described.

3-*Chloro*-5-*bromo*-2-*anilino*-1 : 4-*naphthaquinone*, dark red needles, m. p. 239°, is converted by treatment with sodium sulphide and oxidation of the product by air into 7-*bromo*-ββ-*naphthaphenthiazine*-6 : 11-*quinone* (annexed formula), bluish-green, prismatic crystals, m. p. 325°; the corresponding *sulphoxide*, brownish-red, coarse crystals, m. p. 270°, and the *sulphone*, orange-red, lustrous leaflets, m. p. above 360°, are described. Boiling acetic anhydride and zinc dust convert the quinone into the *triacetyl* derivative of 7-*bromo*-6 : 11-*dihydroxy*-



ββ-*naphthaphenthiazine*, lustrous leaflets, m. p. 299°. 7-*Anilino*-ββ-*naphthaphenthiazine*-6 : 11-*quinone* crystallises in slender, dark violet needles, m. p. 265°; it gives a yellow vat with hyposulphite. 7-p-*Anisidino*-ββ-*naphthaphenthiazine*-6 : 11-*quinone* forms dark violet crystals, m. p. 230°.

3-*Chloro*-2-β-*naphthylamino*-1 : 4-*naphthaquinone*, m. p. 194°, prepared from 2 : 3-dichloro-1 : 4-naphthaquinone and β-naphthylamine, is transformed in the usual manner into 1 : 2-*benzo*-ββ-*naphthaphenthiazine*-6 : 11-*quinone* (annexed formula), dark, greenish-blue, prismatic crystals, m. p. 300°; the corresponding sulphone crystallises in orange-red leaflets, m. p. above 400°. Zinc dust and boiling acetic anhydride transform the quinone into the *triacetyl* derivative of 6 : 11-*dihydroxy*-1 : 2-*benzo*-ββ-*naphthaphenthiazine*, colourless crystals, m. p. 217°. H. W.



Reduction Products of the Hydroxyanthraquinones. V. F. L. Goodall and A. G. Perkin (*J. Chem. Soc.*, 1924, **125**, 470—476).—Hydroxyanthranols can be readily prepared in excellent yield by digesting hydroxyanthraquinones with a boiling 20% solution of stannous chloride in 33% hydrochloric acid. The method is serviceable only in those cases in which anthranol formation has been effected by other methods. With purpurin and purpuroxanthin, reduction is incomplete, whilst quinizarin yields quantitatively deep orange-red crystals of 1 : 4 : 9-trihydroxyanthrone, m. p. 152—154° (A., 1920, i, 745).

The following anthranols have been obtained by this method: 1- and 3-hydroxy-, 3 : 6-, 3 : 7-, and 4 : 8-dihydroxy-anthranols, anthrapurpurin anthranol, and anthragallol anthranol. Deoxyalizarin (3 : 4-dihydroxyanthranol), when acetylated and oxidised with ferric chloride, yields 3 : 4 : 5′ : 6′-*tetrahydroxydianthrone*, small, yellow needles, m. p. 268—270° (decomp.); *hexa-acetyl* derivative, $C_{40}H_{30}O_{12}$, colourless needles, m. p. 236—238°. With alcoholic sulphuric acid, it gives *dihydroxy*-3 : 6′-*diethoxydianthrone*, $C_{32}H_{22}O_6$, small plates, m. p. 271—274°, which on careful oxidation with chromic acid yields alizarin β-ethyl ether, orange needles, m. p. 188—189°. *Tetra-acetyldiethoxydianthranol* has m. p. 248—250°. By treatment with methyl sulphate and alkali the dihydroxydiethoxydianthrone is converted into 3 : 4 : 5′ : 6′-*tetramethoxydianthrone*, colourless needles, m. p. 255—256°. Attempts to convert the tetrahydroxydianthrone into the corresponding helianthrone were unsuccessful. Both deoxyalizarin and tetrahydroxydianthrone are mordant dyes. With bromine in carbon disulphide solution, deoxyalizarin dimethyl ether is converted into 10-bromo-3 : 4-dimethoxyanthranol, from which by the action of dimethylamine or of alcoholic potassium hydroxide only alizarin dimethyl ether is obtained. Acetyldeoxyalizarin, on treatment with nitric acid in alcohol or acetic acid, yields 10-*nitro*-3 : 4-*dihydroxyanthranol diacetate*, $C_{18}H_{13}O_7N$, colourless needles, m. p. 156° (decomp.). The violet colour observed when nitric acid is added to a solution

of deoxyalizarin in sulphuric acid is due to the production of nitrodihydroxyanthrone. R. B.

Derivatives of β-Methylanthraquinone. IV. Nitro Derivatives of β-Methylanthraquinone and some of their Transformation Products. R. EDER, C. WIDMER, and R. BÜTLER (*Helv. Chim. Acta*, 1924, **7**, 341—357).—The nitro-β-methylanthraquinone prepared by Römer and Link by nitration of β-methylanthraquinone (A., 1883, 1138) has been supposed to be 1-nitro-3-methylanthraquinone, on the ground that the hydroxymethylanthraquinone prepared from it, m. p. 177—178°, is identical with the 1-hydroxy-3-methylanthraquinone prepared synthetically by Bentley, Gardner, and Weizmann (T., 1907, **91**, 1626). Repetition of this work shows that the hydroxy compound from nitro-β-methylanthraquinone really has m. p. 181—182° and is identical with synthetic 1-hydroxy-2-methylanthraquinone. The nitro compound is therefore 1-nitro-2-methylanthraquinone. It is converted into α-aminoanthraquinone through the 1-aminoanthraquinone-2-carboxylic acid by boiling the latter with potassium stannite solution. The nitro compound is best prepared by Römer and Link's method; at higher temperatures, red by-products are formed.

Dinitration of β-methylanthraquinone or nitration of 1-nitro-2-methylanthraquinone gives a mixture of two isomerides, the 1 : 5- and 1 : 8-dinitro compounds. 1 : 5-*Dinitro-2-methylanthraquinone* forms yellow needles, m. p. 329—331°, subliming with partial decomposition in white needles; it is soluble in 50 parts of boiling pyridine, 450 of boiling acetic acid, very sparingly soluble in other solvents. By oxidation with chromic acid in boiling nitric acid solution it gives 1 : 5-*dinitroanthraquinone-2-carboxylic acid*, needles, m. p. 337—339°. By distillation of the *silver* salt (a red powder), 1 : 5-dinitroanthraquinone is obtained, m. p. above 350°, giving by reduction 1 : 5-diaminoanthraquinone, m. p. 309—310°, not 319° as given by Noelting and Wortmann (A., 1906, i, 291). Conversion of this into anthrarufin proved its constitution. In a similar manner, the constitution of 1 : 8-*dinitro-2-methylanthraquinone*, m. p. 293—295°, was established. It forms white to pale yellow needles, sparingly soluble in organic solvents, but more soluble than the 1 : 5-isomeride. Attempts to obtain higher nitrated derivatives of β-methylanthraquinone were unsuccessful. (Cf. Schaarschmidt and Stahlschmidt, A., 1913, i, 95.) E. H. R.

Neorobin. P. MASUCCI and G. A. SLOTHOWER (*J. Amer. Pharm. Assoc.*, 1923, **12**, 335—338).—"Neorobin," which is prepared by reduction of chrysarobin with tin and acetic acid, is neither a compound of tin nor an acetate. It is at least 50% more active as a reducing agent than chrysarobin, and can be determined by addition of ammoniacal silver nitrate to its solution in acetone, followed by determination of the reduced silver in the usual way.

CHEMICAL ABSTRACTS.

1 : 2 : 8-Trimethoxy-6-methylanthraquinone and 1 : 2 : 8-Trimethoxy-7-methylanthraquinone. J. L. SIMONSEN (*J. Chem. Soc.*, 1924, **125**, 721—726; cf. *ibid.*, 1921, **119**, 1339).—The

condensation of hemipinic anhydride with *m*-cresol using aluminium chloride and boric acid as condensing agents yields mainly 2′-*hydroxy*-3 : 4-*dimethoxy*-4′-*methyl*-2-*benzoylbenzoic acid*, glistening needles, m. p. 229—230°, which on methylation with methyl sulphate gives 2′ : 3 : 4-*trimethoxy*-4′-*methyl*-2-*benzoylbenzoic acid*, glistening prisms, m. p. 198—199°, a small quantity of a *phthalein*, $C_{24}H_{22}O_6$, m. p. 285—287°, being obtained as a by-product in the condensation. Concentrated sulphuric acid at 150° converts the 2′-hydroxy-3 : 4-dimethoxy-4′-methyl-2-benzoylbenzoic acid into the corresponding anthraquinone, but in poor yield, and from the crude hydroxyanthraquinone 1 : 2 : 8-*trimethoxy*-6-*methylanthraquinone*, fine yellow needles, m. p. 164—165°, was obtained by methylation. With *o*-cresol the condensation gave mainly 2′-hydroxy-3 : 4-dimethoxy-3′-methyl-2-benzoylbenzoic acid, bevelled prisms, m. p. 250—251°, accompanied by considerable quantities of a *phthalein*, $C_{24}H_{22}O_6$, m. p. 237—238°, when a large excess of *o*-cresol was used. Methylation converted the benzoylbenzoic acid derivative into 2′ : 3 : 4-*trimethoxy*-3′-*methyl*-2-*benzoylbenzoic acid*, hexagonal prisms, m. p. 199° (*methyl* ester, prisms, m. p. 153—155°), whilst heating with sulphuric acid gave an almost quantitative yield of the crude hydroxyanthraquinone, which was methylated with difficulty to 1 : 2 : 8-*trimethoxy*-7-*methylanthraquinone*, yellow needles, m. p. 209—210°. R. B.

Phenanthrene Series. XXXV. Transformations of Chlorophenanthrenes. J. SCHMIDT and E. ÄCKERLE (*Ber.*, 1924, **57**, [*B*], 363—369).—An extension of the work of Schmidt and Spoun (A., 1922, i, 665). The preparation of 9 : 9- and 10 : 10-dichloro-2-nitrophenanthrones from 2-nitrophenanthraquinone and phosphorus pentachloride in the presence of benzene is described in detail (the position of the chlorine atoms in these compounds is assigned arbitrarily). 9 : 9-Dichloro-2-nitrophenanthrone is reduced by hydroxylamine hydrochloride or phenylhydrazine to 9-*chloro*-2-*nitro*-10-*hydroxyphenanthrene*, yellow needles, m. p. 223° (*acetate*, m. p. 228°; *benzoate*, m. p. 220°). 10 : 10-Dichloro-2-nitrophenanthrone is converted similarly by hydroxylamine hydrochloride into 10-*chloro*-2-*nitro*-9-*hydroxyphenanthrene*, small, yellow crystals, m. p. 193°. It appears therefore that the halogen atoms of the chloro-2-nitrophenanthrones are retained with unexpected firmness; this view is confirmed by the observation that the α-compound is stable towards molecular silver in the presence of boiling benzene.

4-Nitrophenanthraquinone is converted by phosphorus pentachloride in the presence of benzene into a mixture of 9 : 9-*dichloro*-4-*nitrophenanthrone* (α-compound), pale yellow crystals, m. p. 203°, and 10 : 10-*dichloro*-4-*nitrophenanthrone* (β-compound), m. p. 137°. The former substance is transformed by hydroxylamine hydrochloride or phenylhydrazine into 9-*chloro*-4-*nitro*-10-*hydroxyphenanthrene*, m. p. 203° (*acetate*, pale yellow powder, m. p. 223°; *benzoate*, small, colourless crystals, m. p. 196°). 10-*Chloro*-4-*nitro*-9-*hydroxyphenanthrene* has m. p. 153—154° (*benzoate*, m. p. 188—189°).

4-Nitrophenanthraquinone is converted by phosphorus pentachloride under pressure at 120° into 9 : 9 : 10 : 10-*tetrachloro*-4-*nitrodihydrophenanthrene*, slender, brownish-yellow needles, m. p. 164—165°, which is transformed by phenylhydrazine or molecular silver into 9 : 10-*dichloro*-4-*nitrophenanthrene*, m. p. 136—137°; the chlorine atoms are retained with extraordinary firmness in these compounds, particularly in the latter.

Di-9-*chloro*-2-*nitro*-10-*phenanthryl ether*, $\left(C_6H_4<\underset{CCl}{\overset{C_6H_3(NO_2)}{\overset{|}{\underset{|}{\geqslant}}}}C\right)_2O$, a brown substance which does not melt below 370°, is obtained as a by-product of the action of acetic anhydride on 9-chloro-2-nitro-10-hydroxyphenanthrene. The latter substance is converted by alcoholic ammonia at 160° into 2-*nitrophenanthroxazine*,

$$NO_2\cdot C_6H_3\cdot\overset{|}{C}-O-\overset{||}{C}\cdot C_6H_3\cdot NO_2,$$
$$C_6H_4\cdot C\cdot NH\cdot\overset{|}{C}\cdot C_6H_4$$

which does not melt below 370°. H. W.

Enolisation of Camphor. M. Bredt-Savelsberg, C. A. Heinemann, P. Catharinus, and H. Eibel (*J. pr. Chem.*, 1924, [ii], **107**, 65—86).—The method of Tschugaev and Zerevitinov (A., 1907, ii, 509) for the determination of hydroxyl groups has been applied to a study of the enolisation of camphor. When camphor, which in ether, benzene, or alcohol solution is known to possess the ketonic structure, is brought into contact with a Grignard reagent, enolisation takes place and its extent is determined from the hydrocarbon produced corresponding with the alkyl or aryl group in the Grignard reagent used. Thus magnesium methyl halides give methane, magnesium phenyl bromide gives benzene. The extent of the enolisation depends on a number of factors. (1) The alkyl or aryl group in the Grignard reagent. Equimolecular quantities of camphor and Grignard reagent in ether solution show 29% enolisation with magnesium methyl iodide, 14% with magnesium ethyl iodide, and 25% with magnesium α-naphthyl bromide. In the second case, ethylene is produced as well as ethane, in the ratio of about 3 : 10 at 30°. In amyl ether solution, magnesium phenyl bromide shows 21% enolisation (in ethyl ether solution it was very difficult to determine the benzene formed). (2) The halogen present in the Grignard reagent. With the magnesium methyl halides the enolisation of the camphor increases with the electronegative character of the halogen, from about 14·8% in the case of the iodide to 28·2% with the chloride. (3) The proportions of Grignard reagent and camphor. Excess of Grignard reagent favours enolisation of the camphor. With the proportions ½, 1, 2, and 3 mols. of camphor to 1 mol. of Grignard reagent the enolisation figures were 32·6, 14·9, 16·3, and 16·9%, respectively. (4) The time of reaction. Equilibrium is only reached after a prolonged period. With magnesium methyl iodide, periods of ½, 5, 10, 25, and 40 hours showed enolisation of 13·0, 14·1, 14·9, 30·4, and 44·7%, respectively. (5) The character of the solvent. In amyl ether solution, magnesium methyl iodide enolises camphor to the extent of about 3·6%, against 44·7% in ethyl ether. In a

solvent free from oxygen (benzene) the enolisation is 32·5%. (6) The temperature of reaction. With magnesium methyl iodide the enolisation figures in 10 hours were found to be 6·85% at 0° and 14·9% at 20°. The enolisation of camphor by Grignard reagents explains the low yields of tertiary borneols which have been obtained by the Grignard method, as only the keto-form yields a complex from which tertiary borneols are formed. R. B.

Pyroelectricity of Two Derivatives of Camphor. M. R. Lucas.—(See ii, 224.)

Oxidation of *allo*-Ocimene, Ocimene, and Myrcene. C. J. Enklaar (*Chem. Weekblad*, 1924, **21**, 101—102; cf. A., 1906, i, 377).—A sample of *allo*-ocimene (b. p. 98—102°/32 mm.) on treatment with permanganate in dry acetone at 0° was only partly oxidised. The only oxidation product obtained was a neutral substance, allo-*ocimene oxide*, probably $C_{10}H_{16}O$, b. p. 105°/13 mm., d^{20} 0·909, which is neither aldehyde, ketone, nor glycol. By the action of permanganate on ocimene in acetone solution at 56°, an acid (lead salt, crystallising in rhombs) was obtained; this lead salt is suitable for the identification of the terpene. Myrcene under these conditions yields an acid of which the lead salt crystallises in fine needles, readily distinguishable from the ocimene lead salt. By exhaustive treatment of ocimene with permanganate, a mixture was obtained in which only oxalic acid could be identified. S. I. L.

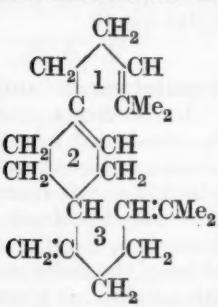
Catalytic Action. IV. A Function of Reduced Copper. S. Komatsu (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 85—91).—When menthol is passed over reduced copper at 320°, besides the expected menthone, some menthene is formed. The copper therefore acts, like thoria, as a dehydrating agent. In the same way, ethyl alcohol yields acetaldehyde and ethylene, and *iso*propyl alcohol (at 300°) gives acetone and propylene. *cyclo*Hexanol is likewise dehydrogenated and dehydrated; *cyclo*hexene, *cyclo*hexanone, di*cyclo*hexyl ether, and water are produced in quantities agreeing with the author's explanation of the reaction, based on the supposition that dehydration takes place in three directions simultaneously. W. A. S.

Higher Terpene Compounds. XX. Sesquiterpenes and Sesquiterpene Alcohols of Camphor Oil. L. Ruzicka and M. Stoll (*Helv. Chim. Acta*, 1924, **7**, 260—270).—So-called heavy camphor oil, b. p. 110—140°/12 mm., contains, besides cadinene and bisabolene, a monocyclic *hydrocarbon*, $C_{15}H_{24}$, which was not more exactly characterised, but forms a very stable *dihydrochloride*, an oil, b. p. 125°/0·3 mm., and a bicyclic *hydrocarbon*, $C_{15}H_{24}$, a colourless oil, b. p. 128—135°/12 mm., which must be of the cadinene type since, when dehydrogenated by boiling with sulphur, it gives cadaline. The sesquiterpene alcohol fraction of camphor oil, b. p. 150—160°/12 mm., gives cadaline when dehydrogenated with sulphur. Purification of this alcohol fraction through the benzoate gives 15% of an alcohol, b. p. 155—160°/12 mm., which agrees in properties with Semmler and Rosenberg's sesquicamphenol (A., 1913,

i, 378). When this purified alcohol was dehydrogenated with sulphur and the product fractionated, the fraction of b. p. 140—145°/12 mm. contained eudaline whilst that of b. p. 150—165°/12 mm. contained cadaline. Camphor oil therefore contains compounds of both cadinene and eudesmol types, and is unique in this respect. The alcohol fraction was separated by means of phthalic anhydride into primary, secondary, and tertiary constituents. The *primary* sesquicamphenol has b. p. 156—158°/12 mm., $[\alpha]_D$ +2·2°, d_4^{18} 0·9568, n_D^{18} 1·5045. It is reduced by hydrogen in presence of platinum black to a *dihydrosesquicamphenol*, $C_{15}H_{23}O$, a colourless, viscous oil, b. p. 152—153°/12 mm., d_4^{22} 0·9150, n_D^{22} 1·4755. From the purified sesquiterpene alcohols a *secondary* sesquicamphenol, b. p. 160—162°/12 mm., $[\alpha]_D$ −5·2°, d_4^{20} 0·9720, n_D^{20} 1·5066, was obtained, which by catalytic reduction gave a dihydrosesquicamphenol, b. p. 150—152°/12 mm., d_4^{15} 0·9510, n_D^{15} 1·4892; whilst from a crude fraction of alcohols, b. p. 140—170°/12 mm., the secondary alcohol appeared to be a mixture of $C_{15}H_{26}O$ and $C_{15}H_{21}O$. One of these alcohols is of the cadinene type. The tertiary alcohol fraction, obtained from the sesquiterpene alcohols purified through the benzoate, had b. p. 156°/12 mm., d_4^{20} 0·9665, n_D^{20} 1·5050, and by dehydrogenation gave both eudaline and cadaline. Two tertiary sesquiterpene alcohols are therefore present in camphor oil.

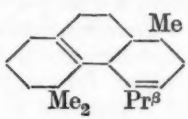
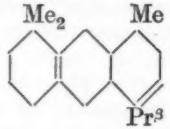
E. H. R.

Higher Terpene Compounds. XXI. Constitution and Isomerisation of α-Camphorene. L. Ruzicka and M. Stoll (*Helv. Chim. Acta*, 1924, **7**, 271—282).—α-Camphorene, the diterpene found by Semmler and Rosenberg in camphor oil (A., 1913, i, 378), is known to be a monocyclic compound related to myrcene, but its constitution has not been determined. Myrcene is probably a mixture of $CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}C(:CH_2){\cdot}CH{:}CH_2$ (I) and $CH_2{:}CMe{\cdot}[CH_2]_3{\cdot}C(:CH_2){\cdot}CH{:}CH_2$ (II), but experiments on its decomposition by ozone indicate that (I) predominates, since only succinic acid was obtained and no trace of glutaric acid. Assuming that myrcene polymerises to α-camphorene by a process similar to the polymerisation of isoprene to dipentene, the annexed formula is obtained for α-camphorene. This formula harmonises with the physical constants of α-camphorene, and with its isomerisation products. When boiled with 95% formic acid, α-camphorene is converted into a *bicyclic diterpene*, a viscous oil, b. p. 192—194°/12 mm., d_4^{14} 0·9086, n_D^{14} 1·5104. The side chain 1 of the above formula has the configuration of a geranyl derivative, and ring closure is to be expected.



More prolonged heating of α-camphorene or of the bicyclic compound with formic acid results in the formation of a *tricyclic diterpene*, b. p. 180—181°/12 mm., d_4^{14} 0·9475, n_D^{14} 1·5201. In the above formula, the ring 2 and the first three carbon atoms of side chain 3 have the dipentene structure, and a wandering of the

double bond into the ring may take place, analogous to the isomerisation of dipentene to α- and γ-terpenes. This would give configurations leading, after ring closure, to the formation of either a phenanthrene or an anthracene derivative,

(III.)  or  (IV.)

By oxidation with manganese dioxide and sulphuric acid the tricyclic α-camphorene gave, besides mellophanic acid, which might result from either formula, pyromellitic acid, which can, as far as is known, only result from the anthracene structure. It is probable, therefore, that the tricyclic compound has structure IV, for which the name isotricyclo*camphorene* is proposed, III being designated tricyclo*camphorene*. By catalytic hydrogenation, only two atoms of hydrogen were taken up, *dihydro*(?iso)tricyclo*camphorene* being formed, a colourless, viscous oil, b. p. 176°/12 mm., d_4^{14} 0·9410, n_D^{14} 1·5118. Oxidation of octahydro-α-camphorene with manganese dioxide and sulphuric acid gave, besides mellophanic acid and pyromellitic acid, terephthalic acid, which is additional evidence in support of the suggested α-camphorene formula. To the two known types of the diterpene series, the abietic acid and dextropimaric acid types, must now be added the camphorene type; in all of these the carbon skeleton is composed of four associated isoprene residues. (Cf. A., 1923, i, 818—819.) E. H. R.

Classification of the Resinic Acids from Conifers. O. Aschan (*Chem.-Ztg.*, 1924, **48**, 149—150).—The acids occurring in pine resins together with some of their derivatives may be divided into three classes, viz., the natural acids such as pimaric and sapic acids; the colophony acids (*iso*pimaric and abietic acids) which are formed by heating the natural sapic acids; and the sylvic acids formed by treating other resinic acids with mineral acids. Of the acids of the first group, the pimaric acids are stable in the air and difficultly soluble in organic solvents, have high melting points, and absorb two atoms of hydrogen in the presence of platinum black; the sapic acids, on the other hand, are very unstable, have low melting points, and dissolve readily in organic solvents. The *iso*pimaric acids are unstable in air, absorb two or four atoms of hydrogen, are fairly easily soluble in hot organic solvents, and melt between 150° and 160°, whilst the abietic acids absorb only two atoms of hydrogen, are difficultly soluble in organic solvents, and melt at about 200°. The true sylvic acids formed by treating the natural acids with hydrochloric or sulphuric acid are stable in the air, absorb four atoms of hydrogen or four hydroxyl groups when treated with permanganate, are difficultly soluble in organic solvents, and have high melting points, whilst the *iso*sylvic acids, formed by splitting off water or hydrogen halide from the corresponding additive products of other resinic acids, are relatively easily soluble in organic solvents and have low melting points. A. R. P.

Synthesis of 7-Ethoxy-4′-dimethylaminoflavone. H. Nägeli and J. Tambor (*Helv. Chim. Acta*, 1924, **7**, 333—336).—Condensation of *p*-dimethylaminobenzaldehyde in alcoholic potassium hydroxide solution with resacetophenone monoethyl ether (2-hydroxy-4-ethoxyacetophenone) gives *2-hydroxy-4-ethoxy-4′-dimethylaminochalkone* (*2-hydroxy-4-ethoxyphenyl 4-dimethylaminostyryl ketone*), red needles, m. p. 149°, giving an intense green fluorescence in organic solvents. The *acetyl* derivative forms yellow needles, m. p. 88°. Treatment of the acetyl compound in carbon tetrachloride solution with pyridine dibromide gave a chalkone dibromide which, without further examination, was converted by alcoholic potassium hydroxide into *7-ethoxy-4′-dimethylaminoflavone*, orange needles, m. p. 183°. Its solution in concentrated sulphuric acid is yellow with a weak green fluorescence; in organic solvents the fluorescence is intense.

2 : 4-*Diethoxyphenyl 4-dimethylaminostyryl ketone*, from resacetophenone diethyl ether, as above, forms bright yellow needles, m. p. 128°. o-*Hydroxyphenyl* p-*dimethylaminostyryl ketone* forms red needles, m. p. 176°. The corresponding p-*hydroxyphenyl* p-*dimethylaminostyryl ketone* forms orange leaflets, m. p. 205°; *acetyl* derivative, brownish-yellow needles, m. p. 136°; *methyl* ether, yellow leaflets, m. p. 126°; *ethyl* ether, orange leaflets, m. p. 113°. 2 : 3-*Dimethoxyphenyl* p-*dimethylaminostyryl ketone* forms brown needles, m. p. 80°, and o-*anisyl* p-*dimethylaminostyryl ketone*, yellow leaflets, m. p. 101°. E. H. R.

Action of the Oxides and the Oxy-acids of Nitrogen on Diphenylene Oxide. H. Ryan and N. Cullinane (*Sci. Proc. Roy. Dubl. Soc.*, 1924, **17**, 321—326).—Whilst diphenylene oxide is unaffected by mixtures of cold nitric and glacial acetic acids, nitric acid in carbon tetrachloride solution, fuming nitric acid in warm acetic acid solution, nitrous fumes, or nitrogen peroxide in carbon tetrachloride or acetic acid, converts it mainly into 3-nitrodiphenylene oxide (cf. Borsche and Bothe, A., 1908, i, 528). Gaseous nitrogen peroxide gives the 3 : 6-dinitro derivative (Mailhe, A., 1912, i, 548), which also results when the mononitro derivative is nitrated. By still more vigorous nitration, first 1 : 3 : 6(?)-*trinitrodiphenylene oxide* (blunt prisms, m. p. 223°), and then 1 : 3 : 6 : 8(?)-*tetranitrodiphenylene oxide* (colourless plates, m. p. 283°) are produced (cf. Mailhe, *loc. cit.*; Borsche and Scholten, A., 1917, i, 390).

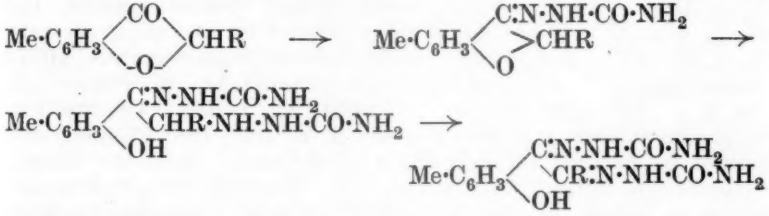
W. A. S.

Valency Requirements of Alkyl [Radicals]. K. von Auwers and G. Wegener (*J. pr. Chem.*, 1923, [ii], **106**, 226—252).—When the silver compound of benzamide is treated with methyl iodide at the ordinary temperature, 52% undergoes change in 11 days, the product affording, with picric acid, ammonium and benzimino methyl ether picrates. When ethyl iodide is used (91% interaction in 5·5 days) the corresponding products are ethyl benzoate, benzonitrile, ammonium picrate, and benzimino ethyl ether dipicrate (?), m. p. 146—147°. When allyl iodide is used, the initial products isolated are benzamide and benzimino *n*-propyl

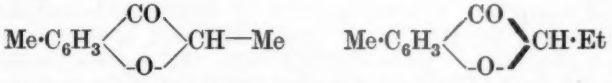
ether (a colourless oil, b. p. 113—116°/12 mm.), the latter with picric acid affording ammonium picrate (cf. Wheeler, A., 1898, i, 185). In none of the above cases were *N*-ethers, described by Wheeler, detected.

s-Formylphenylhydrazine, when treated with methyl iodide in presence of sodium ethoxide, gives a mixture of products; with allyl bromide as alkylating agent the hydrazine is rapidly and quantitatively converted into β-*formyl-α-allyl-α-phenylhydrazine*, white prisms, m. p. 57—58°, b. p. 183°/13 mm. When benzyl chloride is used, β-*formyl-α-benzyl-α-phenylhydrazine* (white prisms, m. p. 108—109°) is formed.

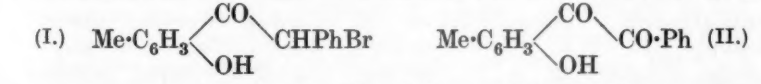
The authors have studied the scission of 4-methyl-1-alkylcoumaranones, using semicarbazide:



The coumaranone (1 mol.) was left in aqueous-alcoholic solution at 45—50° in presence of 2·5 mols. of semicarbazide hydrochloride and sodium acetate and the time required for the initial separation of the disemicarbazone noted. The times (hours) required were as follows: R=Me, 4; R=Et, 14; R=Pr$^{\alpha}$, 4; R=Pr$^{\alpha}$CH$_2$·, 6·5; R=*n*-pentyl, 7·5; R=Ph·CH$_2$, 14·5. These results agree well with those *e.g.* of Meerwein (A., 1920, i, 2), as is evident from the following formulæ:



A phenyl radical (possessing greater valency requirements than an alkyl radical) in position 1 facilitates scission of coumaranones to such an extent that it is impossible to convert (I) into 1-phenyl-



coumaranone satisfactorily, the latter substance being accompanied by (II) and a little *o*-benzoyl-*p*-cresotic acid (produced by the oxidation of 1-phenylcoumaranone). Since coumaranones not alkylated in position 1 cannot be split with semicarbazide, hydrogen must have a lower valency requirement than an alkyl radical. 1 : 1-Dialkylcoumaranones are less readily split by reagents than coumaranone itself, only giving monosemicarbazones with difficulty; this is probably due to steric hindrance. Coumaranones containing the 1-grouping >CR(OR), where R=H or alkyl, are readily split, but this may be attributed to the interaction of the ·OR radical with semicarbazide.

The authors compare and contrast the scission of coumaranones with that of benzoxazoles (Skraup, A., 1919, i, 598) and of phthalides (Teppema, A., 1923, i, 256), from the point of view of valency requirements of the groups present.

A number of new compounds are described: *α-Bromo*-n-*valeryl bromide* is a colourless liquid, b. p. 190°; *α-bromo*-n-*hexanoyl bromide* is a colourless liquid, b. p. 201—210°/ordinary press. (decomp.) or 85—90°/12—13 mm.; *α-bromo*-n-*heptanoyl bromide*, a pale yellow liquid, has b. p. 101—102°/9 mm.; *α-bromopalmityl bromide* is a white solid, charring when heated. These bromides, condensed with *p*-cresol methyl ether (A., 1918, i, 27), give rise to ketones: 3-*α-bromo*-n-*valeroyl*-p-*cresol* forms yellow plates, m. p. 51—52°; 3-*α-bromo*-n-*hexanoyl*-p-*cresol*, yellow needles, has m. p. 30·5—31·5°; 3-*α-bromo*-n-*heptanoyl*-p-*cresol*, yellow needles, has m. p. 49—50°; 3-*α-bromopalmitoyl*-p-*cresol* forms yellow crystals, m. p. 46—47°. The ketones, with alcoholic sodium acetate, afford coumaranones: 4-*methyl*-1-n-*propylcoumaranone*, a yellow oil, has b. p. 133—134°/11 mm., d_4^{20} 1·064, n_{He}^{20} 1·5445; 4-*methyl*-1-n-*butylcoumaranone*, a yellow oil, has b. p. 166—168°/17 mm., and cannot be purified through the semicarbazone, since the disemicarbazone is formed even in the cold; 4-*methyl*-1-n-*pentylcoumaranone*, a yellow oil, has b. p. 175°/18 mm.; 4-*methyl*-1-n-*tetracaidecylcoumaranone* forms waxy white crystals, m. p. 68—69°, and when heated in alcoholic solution with *p*-nitrophenylhydrazine hydrochloride affords the pp-*dinitro-osazone* of p-*cresyl tetracaidecyl ketone*, $OH\cdot C_6H_3Me\cdot C(:N\cdot NH\cdot C_6H_4\cdot NO_2)\cdot C(:N\cdot NH\cdot C_6H_4\cdot NO_2)\cdot C_{14}H_{29}$ +1(or 2)H_2O, red crystals, m. p. 164—165° (with previous softening); 4-*methyl*-1-*benzylcoumaranone*, from 2-hydroxy-4-methylcoumarilic ester, sodium ethoxide, and benzyl chloride, forms white prisms or needles, m. p. 50—51°, b. p. 200—210°/13—14 mm. The benzyl compound is accompanied by 2-*benzoxy*-4-*methylcoumarilic acid*, white needles, m. p. 146—147°, and is converted by *p*-nitrophenylhydrazine hydrochloride into the pp-*dinitro-osazone* of p-*cresyl benzyl diketone*, decomp. 223° (if heated rapidly). 4-*Methyl*-1 : 1-*dibenzylcoumaranone* forms colourless needles or rhombohedra, m. p. 122—123°.

The following were obtained by treating coumaranones with semicarbazide: *disemicarbazone* of p-*cresyl* n-*propyl diketone*, decomp. 212—213° (rapid heating); *disemicarbazone* of p-*cresyl* n-*butyl diketone*, m. p. or decomp. 213—214° (rapid heating); *disemicarbazone* of p-*cresyl* n-*pentyl diketone*, m. p. 208—216°; *disemicarbazone* of p-*cresyl benzyl diketone*, m. p. 222° (rapid heating).

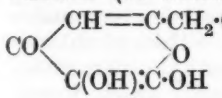
E. E. T.

Hydroxyhydrindone and Chromanone. F. Mayer and L. van Zütphen (*Ber.*, 1924, **57**, [*B*], 618).—The product, m. p. 111°, obtained by the action of aluminium chloride on *o*-β-chloropropionylphenol and considered to be 4-ketochroman (Mayer and van Zütphen, this vol., i, 410) is shown to be 7-hydroxy-α-hydrindone (Knake and Salkowski, A., 1916, i, 820; von Auwers and Hilliger, A., 1917, i, 38).

H. W.

Synthesis of 7-Methoxychromanone. A. E. TSCHITSCHIBABIN (*Ber.*, 1924, **57**, [*B*], 617).—The synthesis of 7-methoxychromanone by Pfeiffer and Oberlin (cf. this vol., i, 413) from resorcinol monomethyl ether and iodopropionic acid had already been effected by Tschitschibabin and Nikitin in 1911 (A., 1911, i, 1007). F. A. M.

The Constitution of Kojic Acid, a γ-Pyrone Derivative formed by *Aspergillus oryzæ* from Carbohydrates. T. YABUTA (*J. Chem. Soc.*, 1924, **125**, 575—587).—Previous work

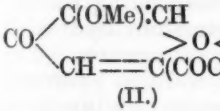


(I.)

(A., 1922, i, 939) has shown that kojic acid (I) is probably the alcohol corresponding with comenic acid. Interconversion by oxidation of kojic acid or reduction of comenic acid has not been accomplished, but both compounds furnish the same 4 : 5-dihydroxy-2-methylpyridine. Kojic acid on treatment with thionyl chloride yields *5-hydroxy-2-chloromethyl-γ-pyrone*, needles, m. p. 166—167°. The latter gives the corresponding *5-benzoyloxy* derivative, prisms, m. p. 117—118°, and the *5-methoxy* derivative, needles, m. p. 119—121°, and on reduction with zinc dust and acetic acid gives allo*maltol* (5-hydroxy-2-methyl-γ-pyrone), prisms, m. p. 166°. *Allo*maltol is distinct from maltol (Brand, A., 1894, i, 270) and from *iso*maltol (Backe, A., 1910, i, 225, 544), the distinction being confirmed by the preparation of the following derivatives. Allo*maltol methyl* ether (5-methoxy-2-methyl-γ-pyrone), prisms, m. p. 70—71°, b. p. (approx.) 93°/0·1 mm.; *benzoyl*allo*maltol* (3-benzoyloxy-6-methyl-γ-pyrone), prisms, m. p. 128—129°; *phenylcarbamate* of allo*maltol*, $NHPh{\cdot}CO{\cdot}C_6H_5O_3$, plates, m. p. 186—188°; *bromo*allo*maltol* (6-bromo-5-hydroxy-2-methyl-γ-pyrone), crystals, m. p. 171—173°. *Benzeneazo*allo*maltol* (6-benzeneazo-5-hydroxy-2-methyl-γ-pyrone), by treating *allo*maltol in solution with diazobenzene acetate, forms reddish-brown needles, no definite m. p.

Oxidation of the following kojic acid derivatives did not give the corresponding comenic acid derivatives: monobenzoyl kojic acid; *monoethyl ether* of *kojic acid* (5-ethoxy-2-hydroxymethyl-γ-pyrone), prepared by the interaction of kojic acid, ethyl *p*-toluenesulphonate, and sodium ethoxide in alcohol, needles, m. p. 110°; *5-ethoxy-2-hydroxymethyl-4-pyridine*, prepared from kojic acid monoethyl ether, and isolated as the *picrate*, needles, m. p. 184—185°; 5-hydroxy-2-chloromethyl-γ-pyrone and its methyl ether; *5-hydroxy-2-iodomethyl-γ-pyrone*, prepared from the corresponding chloro-compound as crystalline plates; *5-methoxy-2-iodomethyl-γ-pyrone*, prisms, m. p. 135—137°.

The following derivatives of comenic acid were prepared, but reduction did not give the corresponding kojic acid derivatives.



(II.)

Benzoylcomenic acid, prisms from alcohol, m. p. 227—228°; *methyl ether* of *comenic acid*, prisms, m. p. 280—282°; *methyl ether* of *methyl comenate*, m. p. 197°; *methyl ether* of *ethyl comenate*, m. p. 156°; the *hydrochloride* of the *methyl ether* of *comenyl chloride* (II), prepared by the

action of thionyl chloride on comenic acid methyl ether, prisms, m. p. 103°; the *methyl ether* of *comenyl chloride*, prepared from the previous compound by the action of sodium acetate, m. p. 148°; *comenamide methyl ether*, prepared by the action of ammonia on (II), needles, m. p. 178°. The catalytic reduction of the methyl ether of comenyl chloride by Rosenmund's method (A., 1918, i, 300; 1921, ii, 320, 392) failed owing to the instability of the pyrone nucleus. *Comenamic acid methyl ether* (5-methoxy-4-pyridone-2-carboxylic acid) was prepared by the action of ammonia on comenic acid methyl ether; *ammonium* salt, needles, m. p. 269°; *hydrochloride*, prisms. Thionyl chloride introduces chlorine into the 4-position of the methyl ether, giving *4-chloro-5-methoxypyridine-2-carboxylic acid chloride*, which Rosenmund's method also failed to reduce. The acid chloride was converted into *4-chloro-5-methoxypyridine-2-carboxylic acid*, prisms, m. p. 209°, into the *amide*, needles, m. p. 207—208°, into the *methyl* ester, prisms, m. p. 167°, and into the *ethyl* ester, prisms, m. p. 140°.

*allo*Maltol methyl ether, prepared either by the methylation of *allo*maltol or by the reduction of 5-methoxy-2-chloromethyl-4-pyrone, when heated with ammonia in a closed tube at 100° gives *5-methoxy-2-methyl-4-pyridone*, needles, m. p. 115°, which gives a *picrate*, needles, m. p. 205—206°. The dimethyl ether of kojic acid, when similarly treated, yields the corresponding pyridine derivative, which distils at 200°/1 mm., and on heating with red phosphorus and hydriodic acid gives 4 : 5-*dihydroxy-2-methyl pyridine*, prisms, decomp. 280°, and crystallising $+1H_2O$ at low temperatures.

Comenic acid when heated with ammonia under pressure gives comenamic acid, which when treated with phosphorus pentachloride and then reduced with tin and hydrochloric acid gives the same 4 : 5-dihydroxy-2-methylpyridine. The dihydroxypicolines obtained thus from both acids gave on methylation the same *5-methoxy*-1 : 2-*dimethyl*-4-*pyridone* ($+3H_2O$), colourless needles, m. p. 98°. This compound is also formed by treating *allo*-maltol methyl ether with methylamine, thus confirming the position of the methyl groups. Comenamic acid on methylation gives similarly *5-methoxy*-1-*methyl*-4-*pyridone*-2-*carboxylic acid* ($+4H_2O$), needles, m. p. 208°. F. G. M.

Action of Sodium Sulphite on Coumarins. B. B. Dey and K. K. Row (*J. Chem. Soc.*, 1923, **125**, 554—564).—Coumarins and many substituted coumarins react readily with sodium hydrogen sulphite to give β-sulphonic acids, *e.g.*,

$$OH\cdot C_6H_4\cdot CH(SO_3Na)\cdot CH_2\cdot CO_2H,xH_2O.$$

These yield halogen and nitro derivatives, which when heated with sulphuric acid give sulphur dioxide and the corresponding *Bz*-substituted coumarins, and when heated with potassium hydroxide solution give the corresponding potassium coumarates. The ethers of coumarinic acid when boiled with sodium hydrogen sulphite solution and then with sodium hydroxide solution give the corresponding ethers of coumaric acid.

Thus coumarin when boiled with aqueous sodium hydrogen sulphite gives *sodium dihydrocoumaric acid* β-*sulphonate*, colourless plates from water, decomp. 175—176° (*potassium*, *barium*, and *calcium* salts described). 6-Nitrocoumarin gives *sodium* 5-*nitrodihydrocoumaric acid* β-*sulphonate*, whilst 3-chloro- and 3-bromocoumarin both give benzfuran-2-carboxylic acid (cf. Fittig, A., 1883, 474). 3 : 6-Dinitrocoumarin gives 5-nitrosalicylaldehyde, whilst *o*-coumaric acid behaves like coumarin itself. 3-Acetylcoumarin gives *sodium* α-*acetyldihydrocoumaric acid* β-*sulphonate*, white crystals, m. p. 163° (decomp.). Sodium dihydrocoumaric acid β-sulphonate when treated in aqueous solution with chlorine gives *sodium* 3 : 5-*dichlorodihydrocoumaric acid* β-*sulphonate* (colourless needles), which on heating alone or with sulphuric acid gives sulphur dioxide and 6 : 8-*dichlorocoumarin*, crystalline nodules, m. p. 160°, subliming at 130—135° in colourless needles. Bromine similarly gives *sodium* 3 : 5-*dibromodihydrocoumaric acid* β-*sulphonate* (plates), which on heating gives 6 : 8-*dibromocoumarin*, needles, m. p. 176°. Iodine gives *sodium* 5-*iododihydrocoumaric acid* β-*sulphonate*, colourless plates, which on heating yields 6-*iodocoumarin*, needles, m. p. 165°.

Sodium 5-nitrodihydrocoumaric acid β-sulphonate on bromination gives *sodium* 3-*bromo*-5-*nitrodihydrocoumaric acid* β-*sulphonate*, colourless plates, decomp. 210°, on iodination *sodium* 3-*iodo*-5-*nitrodihydrocoumaric acid* β-*sulphonate*, and on treatment with fuming nitric acid gives *sodium* 3 : 5-*dinitrodihydrocoumaric acid* β-*sulphonate*.

8-*Bromo*-6-*nitrocoumarin*, colourless needles from acetic acid, m. p. 200°, is obtained by heating the corresponding sodium dihydrocoumaric acid β-sulphonate with sulphuric acid, and on reduction with 5% acetic acid and iron filings gives 8-*bromo*-6-*aminocoumarin*, yellow needles, m. p. 200°. The latter gives an *acetyl* derivative, colourless needles, m. p. 249°, a *benzoyl* derivative, needles from acetic acid, m. p. 217°, a *hydrochloride*, colourless prisms, darkening at 235°, m. p. 246° (decomp.), and a *picrate*, yellow needles, m. p. 180—181° (decomp.). 8-*Iodo*-6-*nitrocoumarin*, similarly prepared, colourless needles, m. p. 249° (decomp.), on reduction gives 8-*iodo*-6-*aminocoumarin*, orange-yellow needles, m. p. 210°, which yields an *acetyl* derivative, needles, m. p. 275° (decomp.). 6 : 8-*Dinitrocoumarin*, similarly prepared, forms yellow needles, m. p. 158°.

The following *o*-coumaric acids were prepared by treating the corresponding sodium dihydrocoumaric acid β-sulphonates with boiling 20% potassium hydroxide solution and then acidifying. The acids on fusion with potassium hydroxide lose carbon dioxide, giving styrene derivatives. 5-*Chlorocoumaric acid*, needles, m. p. 228° (decomp.); 5-*bromocoumaric acid*, needles, m. p. 224° (decomp.); 3 : 5-*dichlorocoumaric acid*, crystals, m. p. 242° (decomp.), *methyl* ester, colourless needles, m. p. 176°; 3 : 5-*dibromocoumaric acid*, needles, m. p. 238° (decomp.), *methyl* ester, needles, m. p. 173°, *ethyl* ester, spear-shaped crystals, m. p. 128°, *acetyl* derivative, needles, m. p. 201°. 5-*Nitrocoumaric acid*, colourless needles,

m. p. 247° (decomp.), *silver* salt, insoluble and orange-coloured, *methyl* ester, colourless needles, m. p. 211°, *acetyl* derivative, needles, m. p. 217°, immediately resolidifying, and melting again at 259°. 3-*Bromo*-5-*nitrocoumaric acid*, colourless needles, m. p. 234° (decomp.), *methyl* ester, needles, m. p. 212°, *ethyl* ester, fern-shaped crystals, m. p. 184°, *acetyl* derivative, needles, m. p. 186° (decomp.). 5-*Nitro*-4-*methylcoumaric acid*, colourless needles, m. p. 219° (decomp.), *silver* salt, deep orange-red, *methyl* ester, needles, m. p. 187°, *ethyl* ester, needles, m. p. 160°; the acid itself, on fusion with potassium hydroxide, gives 5-nitro-2-methoxy-4-methylcinnamic acid, *methyl* ester, needles, m. p. 136°.

The methyl ethers of coumarinic and 5-nitrocoumarinic acids when boiled with 20% sodium sulphite solution were smoothly converted into the ethers of the corresponding coumaric acids.

α-*Naphthacoumaric acid*, prepared from α-naphthapyrone, needles, m. p. 167° (decomp.), *silver* salt, pale yellow. 4-*Nitro*-α-*naphthacoumaric acid*, prepared from 6-nitronaphthapyrone, small crystals, m. p. 179—180° (decomp.), *silver* salt, orange.

An aqueous solution of α-1 : 8-*iso*naphthoxazone when boiled with sodium sulphite and then with potassium hydroxide, and finally neutralised, gave 6-*hydroxyquinoline*-5-β-*acrylic acid*, $OH\cdot C_9H_5N\cdot CH{:}CH\cdot CO_2H$, white powder, m. p. 220° (decomp.); *silver* salt, pale yellow. The acid, when heated with sulphuric acid, gave the original *iso*naphthoxazone. F. G. M.

Fluorescence. J. Tröger and O. Grünthal (*J. pr. Chem.*, 1923, [ii], **106**, 173—202; cf. A., 1923, i, 355).—The authors have prepared a number of arylsulphonearylideneacetonitriles of the type $R\cdot CH{:}C(SO_2R')CN$ (cf. A., 1908, i, 798), and recorded the fluorescence (if any) of their solutions in concentrated sulphuric acid, glacial acetic acid, etc. R=2-hydroxy-1-naphthyl, R′=Ph, lemon-yellow prisms, m. p. 221° (decomp.): this *nitrile* gives an intense green fluorescence in cold glacial acetic acid; the green fluorescence observed in concentrated sulphuric acid becomes blue on standing, probably owing to the formation of 2-benzenesulphonyl-4 : 3-β-naphthapyrone, which results when the yellow compound is heated with acetic anhydride. R=2-hydroxy-1-naphthyl, R′=*p*-tolyl: this *nitrile* [lemon-yellow prisms, m. p. 232° (decomp.)] exhibits fluorescence similar to the last compound and with acetic anhydride affords 2-*p*-toluenesulphone-*p*-naphthapyrone. R=2-hydroxy-1-naphthyl, R′=*p*-chlorophenyl: this *nitrile* [lemon-yellow prisms, m. p. 254° (decomp.)] shows fluorescence as above, and with acetic anhydride gives 2-*p*-chlorobenzenesulphonyl-β-naphthapyrone. R=2-hydroxy-1-naphthyl, R′=*o*-anisyl: this *nitrile* [sulphur-yellow prisms, m. p. 241° (decomp.)] exhibits fluorescence as above and is converted by acetic anhydride into 2-o-*anisylsulphone*-β-*naphthapyrone*, reddish-yellow prisms, m. p. 280° (decomp.). R=2-hydroxy-1-naphthyl, R′=β-naphthyl: this *nitrile* [yellow prisms, m. p. 198° (decomp.)] exhibits fluorescence as above and with acetic anhydride affords 2-β-*naphthalenesulphonylnaphthapyrone*, yellow prisms, m. p. 234° (decomp.). R=2-methoxy-

1-naphthyl, R′=Ph: this *nitrile* (prisms, m. p. 188°) shows the above type of fluorescence. R=2-methoxy-1-naphthyl, R′=*p*-tolyl: this *nitrile* (yellow prisms, m. p. 197°) develops fluorescence slowly in the above solvents, as is the case with the *nitrile* (sulphur-yellow prisms, m. p. 206°) having R=2-methoxy-1-naphthyl and R′=*p*-chlorophenyl. R=2 : 7-dihydroxynaphthyl, R′=*p*-tolyl: this *nitrile* [yellowish-green prisms, m. p. 288° (decomp.)] shows no fluorescence in sulphuric acid solution, owing to the fact that 9-acetoxy-2-*p*-toluenesulphonyl-β-naphthapyrone (m. p. 251°), which results when it is heated with acetic anhydride, is non-fluorescent under similar conditions. The *nitrile* having R=2 : 7-dihydroxynaphthyl and R=Ph forms brownish-green prisms, m. p. 246° (decomp.), and behaves similarly to the tolyl derivative. Other *nitriles* giving non-fluorescent solutions in sulphuric acid are those in which R=*o*-hydroxyphenyl, R′=Ph (white crystals, m. p. 160°), and R=*m*-acetoxyphenyl, R′=*p*-tolyl (grey leaflets, m. p. 134°). The *nitrile* containing R=2 : 5-dihydroxyphenyl, R′=*p*-tolyl [yellow needles, m. p. 224° (decomp.)], develops very little fluorescence and on boiling in alcoholic solution passes into 3-*p*-toluenesulphonyl-6-hydroxycoumarin, the latter substance possessing very slight fluorescent properties. The *nitriles* (canary-yellow prisms, m. p. 159° and 150°, respectively) containing R=2 : 5-dimethoxyphenyl, R′=Ph, and R=2 : 5-dimethoxyphenyl, R′=*p*-tolyl, develop fluorescent effects slowly in acid solution. The *nitriles* containing R=3 : 4-dihydroxyphenyl, R′=*p*-tolyl [yellow prisms, m. p. 183° (decomp.)], and R=3 : 4-methylenedioxy, R′=*p*-tolyl (pale yellow leaflets, m. p. 168°) exhibit no fluorescent effects. On the other hand, when R=2 : 4-dihydroxyphenyl, R′=Ph (yellow prisms, m. p. 237°), marked fluorescence is shown by the *nitrile* in sulphuric acid solution. Moderate fluorescent effects are observed with the *nitrile* having R=2 : 4-dihydroxyphenyl, R′=*p*-tolyl [yellow prisms, m. p. 247° (decomp.)], this nitrile being converted by acetic anhydride into 3-*p*-toluenesulphonyl-7-acetoxycoumarin. Similar properties apply to the *nitrile* in which R=2 : 4-dihydroxyphenyl, R′=*p*-chlorophenyl [sulphur-yellow prisms, m. p. 232° (decomp.)], this compound passing, in boiling alcoholic solution, into 3-*p*-chlorobenzenesulphonyl-7-hydroxycoumarin (m. p. 232°). A sulphuric acid solution of the *nitrile* having R=2 : 4-dihydroxyphenyl, R′=*o*-anisyl (yellow prisms, m. p. 198°) slowly develops fluorescence. The following *nitriles* show no fluorescence: (1) R=2 : 4-dihydroxyphenyl, R′=β-naphthyl, sulphur-yellow prisms, m. p. 253° (decomp.), and (2), R=2 : 4-dimethoxyphenyl, R′=Ph, yellow needles, m. p. 154°.

From the above, it is seen that strongly fluorescent solutions (in concentrated sulphuric acid) are obtained from nitriles possessing a hydroxyl group in the ortho-position to the unsaturated side chain. Other theoretical points are discussed, for which the original should be consulted. E. E. T.

Attempted Syntheses of *meta*-Related Ring Systems. II. F. Reindel and L. Schuberth (*Ber.*, 1924, **57**, [*B*], 369—371; cf. Reindel and Siegel, A., 1923, i, 916).—The action of *m*-xylylene bromide on pyrocatechol, resorcinol, or quinol in alcoholic solution in

the presence of sodium alkoxide yields only mixtures of products which could not be purified satisfactorily. Better results are obtained with the monomethyl ethers, whereby m-*xylenyl di*-o-*anisyl ether*, $C_6H_4(CH_2\cdot O\cdot C_6H_4\cdot OMe)_2$, colourless needles, m. p. 115°, and m-*xylenyl di*-p-*anisyl ether*, quadratic leaflets, m. p. 128°, are isolated; resorcinol methyl ether gives a compound, b. p. 121°/10 mm., which contains halogen. The compounds, however, are not adapted to the production of *meta*-related ring systems, since they cannot be demethylated without extensive decomposition of the molecule. Attempts to replace methyl by more readily eliminable radicals (acetyl, benzoyl, or carbethoxyl) did not lead to the desired result owing to the ready fission of the compounds into their components.

m-Dithiolbenzene is converted by *m*-xylylene bromide and sodium ethoxide in the presence of alcohol and benzene into the *meta*-cyclic *thioether*, $C_6H_4<\begin{matrix}S\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot S\\S\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot S\end{matrix}>C_6H_4$, colourless needles, m. p. 235°. H. W.

Formation of Pyrrole Derivatives from Amides of β-Diketonic Esters. W. Küster and P. Schlack [with E. Erfle and W. Heess] (*Ber.*, 1924, **57**, [*B*], 409—413).—Dicarbonyl derivatives obtained from oxalic esters are not generally suited to the production of pyrrole derivatives by reason of their strongly acidic character. Attempts are described to obtain more successful results from compounds of this type in which the acidity has been diminished by the introduction of groups containing nitrogen.

Acetylpyruvanilide, $CH_2Ac\cdot CO\cdot CO\cdot NHPh$, pale yellow needles, m. p. 140—141 (cf. Mumm and Bergell, A., 1912, i, 936), is readily converted into the corresponding *nitroso* derivative, $C_{11}H_{10}O_4N_2$, dark yellow prisms, m. p. 138°, which could not be caused to react with ethyl acetoacetate to yield a substituted pyrrole. A negative result was also obtained when the diketone and ethyl nitrosoacetoacetate were employed.

Ethyl oxalate condenses with acetmethylanilide in the presence of sodium ethoxide to give *ethoxalylacetmethylanilide*,

$$CO_2Et\cdot CO\cdot CH_2\cdot CO\cdot NMePh,$$

colourless needles, m. p. 75°, b. p. 112°/740 mm. (*copper* salt, $C_{26}H_{28}O_6N_2Cu$, m. p. 112—115°; and *iron* salt, $C_{39}H_{42}O_{12}N_3Fe$). Reduction of a mixture of ethyl nitrosoacetoacetate and ethoxalylacetmethylanilide by zinc dust and glacial acetic acid leads to the formation of *ethyl* 3-*carboxyphenylmethylamido*-4-*methylpyrrole*-2 : 5-*dicarboxylate*, $\begin{matrix}C(CO\cdot NMePh):C(CO_2Et)\\|\qquad\qquad\quad|\\CMe=\!=\!=\!=C(CO_2Et)\end{matrix}>NH$, colourless crystals, m. p. 82°, which is hydrolysed to the corresponding dicarboxylic *acid*, m. p. 126°.

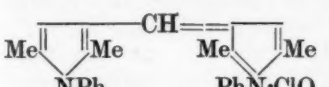
The acid character of ethyl acetylpyruvate, $CH_2Ac\cdot CO\cdot CO_2Et$, is demonstrated by its ability to react with precipitated ferric hydroxide to form the *iron* salt, $C_{21}H_{27}O_{12}Fe$, red, rhombic leaflets. H. W.

Synthesis of Cryptopyrrolecarboxylic Acid. (The Synthesis of the Acid Scission Products of Blood Pigment. I.) H. FISCHER and B. WEISS (*Ber.*, 1924, **57**, [*B*], 602—609; cf. A., 1922, i, 759; 1923, i, 707; this vol., i, 201).—Cryptopyrrolecarboxylic acid has been synthesised in the following way: ethyl 2 : 4-dimethylpyrrole-3-aldehyde-5-carboxylate was condensed with cyanoacetic acid by means of acetic anhydride to give *ethyl* 2 : 4-*dimethyl*-3-[ω-*cyano*-ω-*carboxyvinyl*]*pyrrole*-5-*carboxylate* (yellow needles, m. p. 239°). The latter on reduction gave *ethyl* 2 : 4-*dimethyl*-3-[ω-*cyano*-ω-*carboxyethyl*]*pyrrole*, which forms crystals, m. p. 184°; this was then either (i) heated in a vacuum to give *ethyl* 2 : 4-*dimethyl*-3-ω-*cyanoethylpyrrole*-5-*carboxylate* (m. p. 134°), which was then hydrolysed by concentrated alkali, and after acidification, the crude acid heated with acetic acid and hydriodic acid, the product being cryptopyrrolecarboxylic acid; or (ii) the nitrile-carboxylic acid was (by heating with acetic and hydriodic acids) converted into cryptopyrrolecarboxylic acid. The structure of the acid is thus definitely settled. The following new compounds were also prepared: *ethyl* 2 : 4-*dimethyl*-3-ω-*nitrovinylpyrrole*-5-*carboxylate*, from the corresponding aldehyde and nitromethane or nitroacetic acid, is yellow and has m. p. 231—232°; *ethyl* 2 : 4-*dimethyl*-5-ω-*nitrovinylpyrrole*-3-*carboxylate*, m. p. 165°, was prepared from the isomeric aldehyde and nitromethane. *Ethyl* 2 : 4-*dimethyl*-3-[-*cyano*-ω-*carbethoxyvinyl*]*pyrrole*-5-*carboxylate* (the ethyl ester of the nitrile-carboxylic acid), m. p. 239°, was prepared from the same aldehyde and ethyl cyanoacetate in presence of methylamine; it forms white needles, m. p. 165°, and on hydrolysis yields 2 : 4-*dimethylpyrrole*-3-*aldehyde*-5-*carboxylic acid*, m. p. 230° (decomp.). The following compounds were similarly prepared from cyanoacetic ester and the corresponding aldehyde: 2 : 4-*dimethyl*-3-[ω-*cyano*-ω-*carbethoxyvinyl*]*pyrrole*, crystals, m. p. 121°, giving, when hydrolysed, 2 : 4-*dimethylpyrrole*-3-*aldehyde*, m. p. 126°; *ethyl* 2 : 4-*dimethyl*-5-[ω-*cyano*-ω-*carbethoxyvinyl*]*pyrrole*-3-*carboxylate*, yellow crystals, m. p. 153°; 3-*acetyl*-2 : 4-*dimethyl*-5-[ω-*cyano*-ω-*carbethoxyvinyl*]*pyrrole*, yellow crystals, m. p. 174°; 2 : 4 : 5-*trimethyl*-3-[ω-*cyano*-ω-*carbethoxyvinyl*]*pyrrole*, dark yellow crystals, m. p. 147°; *ethyl* 2 : 4-*dimethyl*-3-[ω-*cyano*-ω-*carbethoxyethyl*]*pyrrole*-5-*carboxylate*, white needles, m. p. 131°; *ethyl* 2 : 4-*dimethyl*-3-[*dicyanovinyl*]-*pyrrole*-5-*carboxylate*, m. p. 214°, from 2 : 4-dimethyl-5-carbethoxypyrrole-3-aldehyde and malononitrile in acetic anhydride; *ethyl* 4-*methyl*-3-*propionyl*-2-*ethylpyrrole*-5-*carboxylate*, from nitrosoacetoacetic ester and dipropionylmethane in glacial acetic acid with the addition of zinc dust, white needles, m. p. 112°; 5-*carbethoxy*-2 : 4-*dimethyl*-3-*pyrrylglyoxylic ester*, m. p. 133°, was prepared from ethyl 2 : 4-dimethylpyrrole-5-carboxylate and methyl cyanocarbonate in presence of hydrochloric acid. Ethyl 2 : 4-dimethyl-3-[cyanoacetyl]pyrrole-5-carboxylate reacts with hydrazine hydrate in presence of sodium ethoxide to give an oily *substance* which shows an intense pyrrole reaction; it forms a *picrate*, and an azo *dye*, m. p. 166°. F. A. M.

Synthetic Experiments with the Fission Products of the Blood Pigments and the Formation of Complex Salts from Dipyrrylmethenes. II. H. FISCHER and M. SCHUBERT (*Ber.*, 1924, **57**, 610—617; cf. preceding abstract).—The synthesis of cryptopyrrole has been modified by heating ethyl 2 : 4-dimethyl-3-acetylpyrrole-5-carboxylate with hydrazine hydrate and sodium ethoxide at 180°. In the synthesis of cryptopyrrole-aldehyde by the Gattermann hydrocyanic acid method, *cryptopyrrole-aldimine* (isolated as the *picrate*, yellow crystals, m. p. 205°) is formed. Attempts to hydrolyse the intermediate product in the synthesis (dicryptopyrrylmethylamine) were unsuccessful, the imine, however, readily yielding cryptopyrrole-aldehyde. The amine, with semicarbazide, affords the semicarbazone of the aldehyde. *5-Chloroacetyl-2 : 3-dimethyl-4-ethylpyrrole*, from hæmopyrrole and chloroacetonitrile, forms colourless needles, m. p. 140°. *5-Dimethylaminoacetyl-2 : 3-dimethyl-4-ethylpyrrole hydrochloride* (colourless needles, m. p. 73°) results from chloroacetylhæmopyrrole and dimethylamine. On submitting hæmopyrrole to the Gattermann synthesis, the product consists of a mixture of *hæmopyrrole-aldimine* (*picrate*, m. p. 200°, decomp. 195—200°), and *C-dihæmopyrrylmethylamine* (*aminodihæmopyrrylmethane*), which forms colourless needles, m. p. 150°. The hæmopyrrole-aldimine, when boiled in aqueous suspension, gives *5-formyl-2 : 3-dimethyl-4-ethylpyrrole*, colourless needles, m. p. 85° (*semicarbazone*, colourless crystals, m. p. 195°). The aldehyde, with hot concentrated hydrochloric acid, yields violet-red crystals of *bis-[2 : 3-dimethyl-4-ethylpyrryl]methene hydrochloride*, m. p. 215°. From phonopyrrolecarboxylic ester (Gattermann synthesis), *methyl hæmopyrrolecarboxylate aldimine hydrochloride* was obtained as colourless needles, m. p. 173°. In a similar manner, cryptopyrrolecarboxylic acid yielded *cryptopyrrolecarboxylic acid aldimine hydrochloride* as colourless needles, m. p. 208°, which on hydrolysis yielded *5-formyl-2 : 4-dimethylpyrrole-3-propionic acid*, yellowish-brown needles, m. p. 151° (*semicarbazone*, m. p. 223°). The cryptopyrrolecarboxyaldehyde, on heating with dilute hydrochloric acid, yields red needles of *bis-[2 : 4-dimethyl-3-carboxyethylpyrryl]methene hydrochloride*, m. p. 235°. Cryptopyrrolecarboxy-aldehyde condenses with cryptopyrrole in presence of hydrochloric acid to give reddish-brown needles of *[2 : 4-dimethyl-3-carboxyethylpyrryl]-[2 : 4-dimethyl-3-ethylpyrryl]methene hydrochloride*, m. p. 215°. The following complex salts of *bis-*[2 : 4-dimethyl-3-carbethoxypyrryl]methene were prepared : *copper*, *nickel*, *cobalt*, and *zinc*; the *nickel*, *cobalt*, and *zinc* complex salts of *bis-*[2 : 4-dimethylpyrryl]methene were also made. F. A. M.

Di-β-pyrrylmethenes. I. H. FISCHER and K. S. SMEYKAL (*Ber.*, 1924, **57**, [*B*], 544—550).—The condensation of ethyl 2 : 5-dimethylpyrrole-3-carboxylate with formic acid in presence of perchloric acid affords a substance, $C_{13}H_{17}N_2 \cdot ClO_4$, orange needles, decomp. 220—230°, and possessing marked sternutatory properties. It appears to be identical with the *perchlorate* of the product obtained by Piloty (A., 1915, i, 461) by condensing 2 : 5-dimethylpyrrole

with 3-formyl-2 : 5-dimethylpyrrole, which appears to be *di*-3-(2 : 5-*dimethylpyrryl*)*methene*. It was obtained also by condensing 2 : 5-dimethylpyrrole with formic acid in presence of perchloric acid. The free *base* forms orange needles charring above 200°. The *hydrochloride* forms long, red needles, the *sulphate*, small, reddish-brown needles. Ethyl 1-phenyl-2 : 5-dimethylpyrrole-3-carboxylate condenses with formic acid in presence of perchloric acid to give the *perchlorate* of a substance, $C_{25}H_{25}N_2 \cdot ClO_4$, presumably *di*-3-(1-*phenyl*-2 : 5-*dimethylpyrryl*)*methene* (annexed formula), which forms reddish-brown leaflets, m. p. 245° (decomp.).



Diethyl 1-hydroxy-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate condenses with formic acid in presence of perchloric acid to give long, red needles of the perchlorate of a substance, decomposing at 210—215°, of the formula $C_{13}H_{17}O_6N_2Cl$, probably the *perchlorate* of di-3-(1-hydroxy-2 : 5-dimethylpyrryl)methene. Ethyl 2 : 5-dimethylpyrrole-4-aldehyde-3-carboxylate undergoes auto-condensation when heated with strong hydrochloric acid to give a *hydrochloride*, red needles, m. p. 181°. The perchlorate, $C_{10}H_{23}N_2 \cdot ClO_4$, appears to be that of *ethyl* 2 : 5 : 2′ : 5′-*tetramethyldi*-β-*pyridylmethene*-4-*carboxylate*, the base being a yellow powder charring at 220—230°. The mother-liquors contain a small amount of the base previously obtained from ethyl 2 : 5-dimethylpyrrole-3-carboxylate. F. A. M.

Catalytic Hydrogenations under Pressure in the Presence of Nickel Salts. VIII. Compounds of the Indole Series. J. von Braun, O. Bayer, and G. Blessing (*Ber.*, 1924, **57**, [*B*], 392—403).—An extension of previous work (A., 1923, i, 835; this vol., i, 426). Indole resembles quinoline in that hydrogenation takes place primarily in the heterocyclic nucleus. The presence of substituents in this nucleus increases its resistance to reduction, and causes hydrogenation to occur to a greater or less extent in the benzenoid half of the molecule. As in the quinoline series, this tendency can be balanced by the introduction of substituents into the benzenoid nucleus.

Hydrogenation of the indoles was effected in decahydronaphthalene solution, generally at 220—250°. The reaction usually comes to an end before the calculated volume of hydrogen has been absorbed and, when this is the case, ammonia is also formed.

The pyrrole ring is not completely stable under the conditions of hydrogenation and yields fully hydrogenated indoles (see below) and *o*-alkylanilines, among which, o-iso*propylaniline*, b. p. 95°/13 mm., d_4^{12} 0·9760 (*hydrochloride*, m. p. 182°; *picrate*, m. p. 160°; *acetyl* derivative, m. p. 70°; *phenylthiocarbamide* compound, m. p. 129—130°), does not appear to have been described previously.

Indole, when hydrogenated at 225° until further absorption of gas does not occur, yields 8% of unchanged material and 66% of basic substances, whereas the remainder suffers more complete degradation accompanied by the production of ammonia. The

bases consist of perhydroindole (octahydroindole), a colourless liquid with an odour of hemlock, b. p. 170—171°/760 mm., d_4^{17} 0·8845 [Willstätter and Jacquet (A., 1918, i, 392) give b. p. 182—183°/720 mm., 65°/12 mm., d_4^{21} 0·9947], which yields a chloroplatinate, m. p. 238—239° [Willstätter and Jacquet, m. p. (indefinite) 172—173°]; a *picrate*, m. p. 189—190° (Willstätter and Jacquet, m. p. about 137—138°); a quaternary *iodide*, m. p. 234° (decomp.), and a *benzenesulphonyl* derivative, m. p. 121—122°; also *o*-ethylaniline, b. p. 209—210°/760 mm., d_4^{21} 0·9769 (*hydrochloride*, m. p. 191°; *picrate*, m. p. 194—195°; *acetyl* derivative, needles, m. p. 113°; *benzoyl* derivative, m. p. 146°; *phenylthiocarbamide* compound, needles, m. p. 124°; *benzenesulphonyl* derivative, m. p. 101—102°). 2 : 3-Dihydroindole can readily be prepared by the partial hydrogenation of indole at 180°.

[In part with G. LEMKE.]—2-Methylindole is converted by hydrogen at 220° into a mixture of 2-*methyloctahydroindole* and 2-*methyl*-4 : 5 : 6 : 7-*tetrahydroindole*. The former compound is a colourless liquid with a pronounced basic odour, b. p. 62°/12 mm., d_4^{3} 0·9142; it gives a *picrate*, pale yellow prisms, m. p. 192—193°, and a *benzenesulphonyl* derivative, m. p. 110—112°. The corresponding quaternary *iodide*, m. p. 196°, is decomposed by treatment with silver oxide and subsequent distillation into an apparently homogeneous, unsaturated *base*, $NMe_2 \cdot C_6H_8 \cdot CH{:}CHMe$ or $C_6H_9 \cdot CH_2 \cdot CHMe \cdot NMe_2$, b. p. 80—81°/13 mm., d_4^{15} 0·8603, which yields a *picrate*, m. p. 129—130°, and a quaternary *iodide*, m. p. 187—188°. When the latter compound is treated with silver oxide and the product is distilled, *propenyltetrahydrobenzene*, $C_6H_9 \cdot CH{:}CHMe$, b. p. 161°, d_4^{17} 0·8285, $n_D^{17·6}$ 1·4837, is obtained. 2-Methyl-4 : 5 : 6 : 7-tetrahydropyrrole is a colourless liquid, b. p. 105°/13 mm., d_4^{10} 0·9871, which gives all the reactions characteristic of pyrroles.

3-Methylindole yields 3-*methyl*-4 : 5 : 6 : 7-*tetrahydroindole*, b. p. 105°/12 mm., d_4^{14} 0·9698, and 3-*methyloctahydroindole*, a mobile liquid, b. p. 70°/12 mm., d_4^{3} 0·8908 [*hydrochloride*, m. p. 260° (decomp.); *picrate*, m. p. 195—196°; *quaternary iodide*, $C_{11}H_{22}NI$, m. p. 190°; *benzenesulphonyl* derivative, colourless crystals, m. p. 129—130°].

1 : 2-Dimethylindole is rapidly hydrogenated at 200° to a mixture of somewhat unstable 1 : 2-*dimethyl*-4 : 5 : 6 : 7-*tetrahydroindole*, b. p. 108°/12 mm., d_4^{20} 0·9815, and 1 : 2-*dimethyloctahydroindole*, a colourless liquid with an odour of hemlock, b. p. 71°/12 mm., d_4^{20} 0·8822, which suffers partial dehydrogenation when boiled. It yields a methiodide, m. p. 197° (also obtained from 2-methyloctahydroindole), a very hygroscopic *hydrochloride*, a *chloroplatinate*, decomp. 220°, and a *picrate*, m. p. 149—150°.

2 : 5-Dimethylindole is slowly and incompletely hydrogenated at 250°. It gives small amounts of 2 : 5-dimethyloctahydroindole, which is characterised as the *benzenesulphonyl* derivative, m. p. 114°, and, preponderatingly, *o-propyl-p-toluidine*, a colourless liquid, b. p. 98—99°/13 mm., d_4^{12} 0·9666. The latter substance gives a *benzenesulphonyl* derivative, m. p. 104°, a *picrate*, m. p. 201°, a *hydrochloride*, m. p. 195°, a *benzoyl* derivative, m. p. 174—175°,

and a *phenylthiocarbamide* compound, m. p. 146°; the amine is converted by boiling its diazotised solution into o-*propyl*-p-*cresol*, b. p. 97°/13 mm., d_4^{22} 1·018.

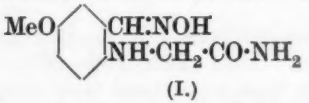
2 : 4 : 7-*Trimethylindole*, a colourless liquid which rapidly darkens in colour, b. p. 158—159°/13 mm., is prepared by the condensation of *p*-xylylhydrazine with acetone and treatment of the product with zinc chloride at 160°. It is hydrogenated to 2-*propyl*-3 : 6-*dimethylaniline*, b. p. 107—110°/13 mm., d_4^{21} 0·9680. The corresponding *picrate*, m. p. 184°, the non-crystalline *hydrochloride*, and the brownish-yellow *chloroplatinate*, decomp. 178°, are described.

H. W.

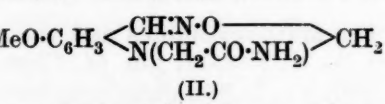
The Methoxyindoles and their Derivatives. K. G. Blaikie and W. H. Perkin, jun. (*J. Chem. Soc.*, 1924, **125**, 296—335).—2-Nitro-5-, -3-, and -6-methoxytoluenes were condensed with ethyl oxalate in presence of potassium ethoxide to form the corresponding nitromethoxyphenylpyruvic acids. 2-*Nitro*-5-*methoxyphenylpyruvic acid* forms yellow needles, m. p. 128°, and gives a *phenylhydrazone*, yellow prisms, m. p. 151—152° (decomp.). 2-*Nitro*-3-*methoxyphenylpyruvic acid* crystallises from acetic acid in yellow prisms, m. p. 118—145°, containing the solvent, which is lost at 100°, leaving the acid as an opaque, pale yellow powder, m. p. 161—162°. The *phenylhydrazone* forms yellow needles, m. p. 159° (decomp.). 2-*Nitro*-6-*methoxyphenylpyruvic acid* forms yellow, indefinite crystals containing benzene, m. p. 47—55°, which retain the solvent after several days in a vacuum. The *phenylhydrazone* forms yellow needles, m. p. 173—174° (decomp.). On oxidation with alkaline hydrogen peroxide, the above nitromethoxyphenylpyruvic acids yield, respectively, 2-*nitro*-5-*methoxyphenylacetic acid*, faintly brown needles, m. p. 176°; 2-*nitro*-3-*methoxyphenylacetic acid*, colourless needles, m. p. 137—138°; and 2-*nitro*-6-*methoxyphenylacetic acid*, bright yellow needles, m. p. 172°. On reduction with ammoniacal ferrous sulphate, the nitromethoxyphenylpyruvic acids give good yields, respectively, of 5-*methoxyindole*-2-*carboxylic acid*, colourless needles, m. p. 196—197° (decomp.) (*ethyl* and *methyl* esters, colourless needles, m. p. 156° and 177°, respectively); 7-*methoxyindole*-2-*carboxylic acid*, colourless needles, m. p. 182° (decomp. at 220—225°) (*ethyl* ester, flat, colourless needles, m. p. 114°; *methyl* ester, colourless plates, m. p. 129°); and 4-*methoxyindole*-2-*carboxylic acid*, colourless needles, m. p. 234—235° (decomp.) (*methyl* ester, colourless plates, m. p. 143·5°; *ethyl* ester, colourless needles, m. p. 161·5°). The above acids lose carbon dioxide on heating, with formation, respectively, of 5-, 7-, and 4-methoxyindoles. 5-*Methoxyindole* forms colourless needles, m. p. 55°, b. p. 176—178°/17 mm., slightly volatile in steam. It forms a *picrate*, $C_{15}H_{12}O_8N_4$, bright red needles, m. p. 145°, and a 1-*acetyl* derivative, colourless, prismatic crystals, m. p. 82°, b. p. 210—211°/25 mm. Two *nitro*-1-*acetyl*-5-*methoxyindoles* (*a*) light brown, flat needles, m. p. 149°, and (*b*) brown plates, m. p. 213—214°, are described, and afford, on hydrolysis, *nitro*-5-*methoxyindoles* (*a*) yellow needles, m. p. 144°, (*b*) m. p. 144° (mixed m. p. 112°), respectively. Application of the Tiemann-

Reimer reaction to 5-methoxyindole produced a mixture of *5-methoxyindole-3-aldehyde*, m. p. 173°, and *3-chloro-6-methoxyquinoline*, m. p. 73—74°. *7-Methoxyindole* forms a colourless syrup, b. p. 157°/17 mm. (*picrate*, $C_{15}H_{12}O_8N_4$, m. p. 156°). *7-Methoxyindole-3-aldehyde*, m. p. 159—160°, *3-chloro-8-methoxyquinoline*, m. p. 84·5°, and *4-methoxyindole*, m. p. 69·5° (*picrate*, m. p. 159—160°), are described.

5-Methoxyindole was also synthesised as follows: 2-amino-5-methoxybenzaldoxime was condensed with chloroacetamide, with formation of *4-methoxy-2-aldehydophenylglycineamide oxime* (I), yellow plates, m. p. 196° (decomp.). The *formyl* derivative (II)



(I.)

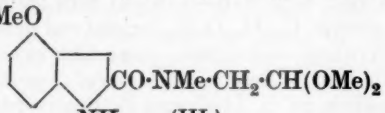


(II.)

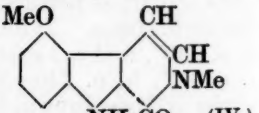
forms bright yellow needles, m. p. 233°. The oxime was hydrolysed to the *oxime* of *4-methoxy-2-aldehydophenylglycine*, pale yellow needles, m. p. 178° (slow decomp.), which was converted by the action of sulphurous acid into *4-methoxy-2-aldehydophenylglycine*, bright orange prisms, m. p. 183° (decomp.) (*phenylhydrazone*, yellow needles, m. p. 175—176°), and this, on heating with sodium acetate and acetic anhydride, yielded 1-acetyl-5-methoxyindole, from which the 5-methoxyindole was obtained on hydrolysis.

α-Ketobutyric acid p-*methoxyphenylhydrazone*, yellow plates, m. p. 105°, yields the *ethyl* ester of *5-methoxyscatole-2-carboxylic acid*, colourless needles, m. p. 151—152°, on treatment with alcoholic sulphuric acid. The free acid forms colourless needles, m. p. 200—201° (decomp.), and the *methyl* ester, colourless plates, m. p. 156°. In the same way, *α-ketobutyric acid* o-*methoxyphenylhydrazone*, pale yellow plates, m. p. 112° (*ethyl* ester, yellow prisms, m. p. 59—60°) is converted into *7-methoxyscatole-2-carboxylic acid*, colourless needles, m. p. 222—223° (decomp.) (*methyl* ester, colourless plates, m. p. 144—145°). The above methoxyscatolecarboxylic acids lose carbon dioxide on heating, with formation, respectively, of *5-methoxyscatole*, plates, m. p. 66° (*picrate*, m. p. 151—152°) and *7-methoxyscatole*, a yellow oil, b. p. 170°/20 mm. (*picrate*, m. p. 156°). The methoxy-indoles and -scatoles give deep colorations with a pine shaving moistened with hydrochloric acid, and characteristic colours, intensified in the case of the indoles by the addition of nitrite, with a solution of *p*-dimethylaminobenzaldehyde in aqueous-alcoholic hydrochloric acid (Ehrlich's reagent).

The action of alcoholic hydrogen chloride on *4-methoxyindole-2-carboxydimethylacetalylmethylamide* (III) (needles, m. p. 112°)



(III.)

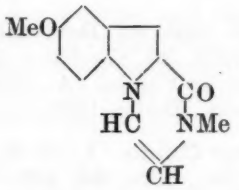


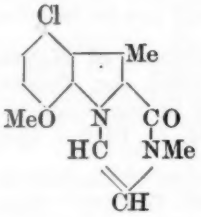
(IV.)

leads to the formation of *9-methoxy-3-keto-4-methyl-3 : 4-dihydro-4-carboline* (IV), needles, m. p. 250°, whilst *5-methoxyindole-2-carb-*

oxydimethylacetalylmethylamide (colourless plates, m. p. 159°) yields about equal proportions of 10-*methoxy*-3-*keto*-4-*methyl*-3 : 4-*dihydro*-4-*carboline*, colourless needles, m. p. 280°, and 10-*methoxy*-5-*keto*-4-*methyl*-4 : 5-*dihydroindolediazine*(1 : 4) (V), colourless, prismatic needles, m. p. 243°.

(V.)





(VI.)

7-*Methoxyindole*-2-*carboxydimethylacetalylmethylamide*, a syrup, yields about 4 parts of 12-*methoxy*-3-*keto*-4-*methyl*-3 : 4-*dihydro*-4-*carboline*, pale yellow plates, m. p. 250°, to 1 part of 12-*methoxy*-5-*keto*-4-*methyl*-4 : 5-*dihydroindolediazine*(1 : 4), four-sided prisms (hydrated), m. p. 135° (anhydrous). 5-*Methoxyindole*-2-*carboxyacetalylamide*, colourless prisms, m. p. 151—152°, yields on the same treatment only 10-*methoxy*-5-*keto*-4:5-*dihydroindolediazine*(1:4) microscopic plates, sintering at 265°, m. p. 280°, whilst 5-*methoxyindole*-2-*carboxyacetalylmethylamide*, colourless needles, m. p. 127°, yields equal quantities of the above carboline (m. p. 280°) and indolediazine (m. p. 243°). The direction of ring formation is thus dependent on the presence or absence of the methyl group in the acetalylamide chain (cf. T., 1922, **121**, 1875). The product derived similarly from 7-methoxyscatole-2-carboxylic acid contained chlorine (apparently introduced in preparing the acid chloride), and was probably 9-*chloro*-12-*methoxy*-5-*keto*-4 : 7-*dimethyl*-4 : 5-*dihydroindolediazine*(1 : 4) (VI), colourless, striated needles, m. p. 109°. It gave no colour reactions with aldehydes.

2-*Nitro*-α-*methoxycinnamic acid*, pale yellow clusters of needles, m. p. 164—165°, is obtained by methylation of the condensation product from *o*-nitrotoluene and ethyl oxalate in presence of sodium ethoxide (*methyl* ester, m. p. 67°). 2-*Amino*-α-*methoxycinnamic acid* loses acetic acid of crystallisation at 100°, forming a pale yellow, opaque powder, m. p. 167° (decomp.) (*methyl* ester, m. p. 60—61°). When treated with cold, concentrated sulphuric acid, boiled with 10% hydrochloric acid, or heated above its m. p., the acid is decomposed into methyl alcohol and indole-2-carboxylic acid. In the same way, by the methylation of metallic derivatives of ethyl nitromethoxyphenylpyruvates, 2-*nitro*-α : 5-*dimethoxycinnamic acid*, yellow needles, m. p. 198—200° (decomp.) (*methyl* ester, m. p. 113—114°; *ethyl* ester, m. p. 74·5°), and 2-*nitro*-α : 3-*dimethoxycinnamic acid*, colourless needles, m. p. 202° (decomp.) are produced. 2-*Amino*-α : 5-*dimethoxycinnamic acid* separates from acetic acid in colourless needles containing the solvent, which is lost at 100°, leaving the acid as a pale yellow, opaque powder, m. p. 173—174° (*methyl* ester, m. p. 81°). 2-*Amino*-α : 3-*dimethoxycinnamic acid* loses acetic acid of crystallisation on standing in air,

is then yellow, and has m. p. 139° (decomp.). Both the above amino-acids decompose on heating into methyl alcohol and the corresponding methoxyindole-2-carboxylic acids. Scatole-2-carboxylic acid can be obtained by a similar synthesis from α-keto-β-*o*-nitrophenylbutyrate, but the corresponding methoxy derivatives could not be isolated. F. G. W.

Constitution of Naphtholisatin and its Derivatives. N. DĂNĂILĂ (*Bul. Soc. Româna Stiin.*, 1923, **26**, 87—95).—A question of priority in connexion with a paper by Cândea (A., 1923, i, 246; cf. Dănăilă, A., 1916, i, 497, and Dissert., Berlin, 1909). R. B.

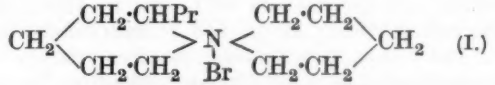
Oxidation of Carbazole by Silver Oxide. G. E. K. BRANCH and W. W. HALL (*J. Amer. Chem. Soc.*, 1924, **46**, 438—445).—In continuation of previous work on this subject, the authors have obtained three fractions B, E, and A (cf. A., 1921, i, 56). E, $C_{36}H_{27}ON_3$ (?), is a white powder, m. p. 189—197° (with charring), which reacts with bromine to give a bromide (?), m. p. 117—125°. It reacts with nitric oxide, and affords two nitroso derivatives, yellow solids, m. p. 216° (decomp.) and 228° (decomp.), respectively. Sulphuric acid converts it into an isomeric *substance*, m. p. 250°. A is a yellow powder affording a bromo derivative, m. p. 85—100°. E is considered to be an hydroxymonocarbazyldibiphenylenehydrazine in which two or three of the carbazole rings are reduced to diphenylamine nuclei, whilst B (which affords a bromo derivative, m. p. 230—245°) is an intermediate in the formation of E, the latter being formed by the combination of the reduced B radicals and the carbazyl nuclei. A. B. S.

The Chemistry of Carbazole. H. LINDEMANN (*Ber.*, 1924, **57**, [*B*], 555—559).—A method is described for preparing 3-nitrocarbazole from carbazole, using glacial acetic acid, sodium nitrite, and nitric acid. 3-Nitro-9-nitrosocarbazole, first obtained, when hydrolysed with alcoholic 40% potassium hydroxide, gives 3-nitrocarbazole, together with about 4% of an isomeride (1-nitrocarbazole ?) (yellow needles, m. p. 187°); the nitro compound (m. p. 164°), hitherto described as the 1-nitro compound, must therefore be either the 2- or 4-*nitrocarbazole* (cf. A., 1909, i, 961). 3-*Nitro*-N-*methylcarbazole* (yellow needles, m. p. 173°), and 3-*nitro*-N-*ethylcarbazole* (yellow needles, m. p. 128°) were prepared by alkylation of the 3-nitro compound. The nitro-*N*-methyl compound when reduced afforded 3-*amino*-9-*methylcarbazole*, grey needles, m. p. 174°. Its *salts* with mineral acids are soluble in water and give *acetyl* and *benzoyl* derivatives, m. p. 210° and 211°, respectively. 3-*Amino*-N-*ethylcarbazole* forms white needles, m. p. 113—114° (*acetyl* derivative, m. p. 190°; *benzoyl* derivative, m. p. 180°).

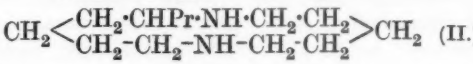
3-Nitro-9-ethylcarbazole, m. p. 128°, does not agree in its properties with the product obtained by Delétra and Ullmann (A., 1904, i, 272) (cf. also Stevens and Tucker, T., 1923, **123**, 2140) from 2-amino-4-nitro-*N*-ethyldiphenylamine; the latter substance, obtained by reducing the corresponding dinitro compound with sodium sulphide, forms red crystals melting at 76°. On treatment

with nitrous acid the corresponding diazonium compound, *2(phenylmethylamino)5-nitrophenyldiazonium nitrate*, was obtained in the form of very stable yellow needles exploding at about 118°. All attempts to convert it into 3-nitro-*N*-methylcarbazole were unsuccessful. F. A. M.

Cyclic bis-Imines and their Decomposition. IV. J. von Braun and J. Pohl (*Ber.*, 1924, **57**, [*B*], 480—484).—Coniine (2 mols.) and αε-dibromopentane interact at water-bath temperatures to give a solid product, probably in accordance with the equation: $2C_8H_{16}>NH+Br[CH_2]_5Br=C_8H_{16}>N\cdot HBr+C_8H_{16}N[CH_2]_5Br$. On further warming there results the hygroscopic quaternary *bromide*, $C_{13}H_{26}NBr$ (I), m. p. 228°. The latter, when heated with ammonia at 200°, is partly converted into the *bis-imine* (II), a colourless oil, b. p. 145—146°/11 mm., d_4^{18} 0·89.



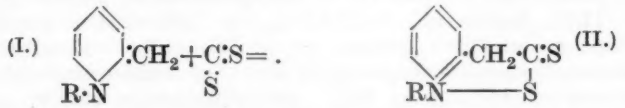
(I.)



(II.)

The *picrate*, *hydrochloride*, and *chloroplatinate* are oily. The *dimethiodide* yields a solid *chloroplatinate*, m. p. 248°. A 40-g. frog is completely paralysed by 0·005 g. of the bis-imine in 3—4 minutes, whilst the same dose of coniine requires about 39 minutes to produce paralysis. F. A. M.

Reactions of *N*-Alkyl-methylenedihydro-pyridines and -quinolines. W. Schneider, K. Gaertner, and A. Jordan (*Ber.*, 1924, **57**, [*B*], 522—532; cf., A. 1921, i, 878).—*N*-Alkyl-α-(or γ-)methylenepyridanes (cf. Decker, A., 1905, i, 667), which are formed on treating quaternary salts of α- or γ-methylated pyridines or quinolines with alkali, are capable of combining directly with either carbon disulphide, phenylcarbimide, or phenylthiocarbimide to form crystalline products. In the case of α-picoline alkiodides, it is suggested that the methylene base (I) reacts thus:



(I.) (II.)

so that the product (II) would be the betaine of *N*-alkyl-α-pyridyldithioacetic acid; whilst the thiocarbimide additive product of the methylene base would have the structure (III) and its salts the

(III.) (IV.)

structure (IV), the carbimide additive compounds having analogous

formulæ which would agree with the ready oxidation of both sulphur and oxygen compounds by cold neutral permanganate, whilst in acid solution they are only slowly oxidised.

N-Methyl-α-methylenedihydropyridine was prepared by treating α-picoline methosulphate with alkali and extracting with ether; on treating the yellow ethereal solution with carbon disulphide, yellow leaflets of the *additive* compound, $C_8H_5NS_2$, were formed which charred at 175° and had m. p. 186°. The *phenylthiocarbimide* (III) forms dark red crystals, m. p. 153°. It is soluble in dilute acids to give pale yellow solutions of the salts (IV), from which the compound is reprecipitated by alkalis. The *hydriodide* forms colourless needles, m. p. 160°, the *picrate*, yellow needles, m. p. 156°. The *phenylcarbimide* forms yellow needles, m. p. 172° (*picrate*, yellow needles, m. p. 173°). N-*Ethyl*-α-*methylenedihydropyridine* gave the following derivatives: *carbon disulphide additive* compound, yellow leaflets, char at 170°, m. p. 180°; *phenylthiocarbimide*, dark red crystals, m. p. 143°; *hydriodide*, m. p. 177°, *picrate*, m. p. 113°; *phenylcarbimide*, needles, m. p. 172°. N-*Benzyl*-α-*methylenedihydropyridine* (from α-picoline benzochloride) gave the following derivatives: *phenylthiocarbimide*, red crystals, m. p. 189°; *picrate*, m. p. 150°; *phenylcarbimide*, yellow crystals, m. p. 192°; *picrate*, m. p. 126°. The following are derivatives of *methylene-anhydro bases from* s-*collidine alkiodides*: (i) *methiodide*: *phenylthiocarbimide*, yellowish-brown crystals, m. p. 185°; *phenylcarbimide*, yellow, m. p. 188°; (ii) *ethiodide*: *phenylthiocarbimide* compound, yellowish-brown, m. p. 190°; *phenylcarbimide*, bright yellow, m. p. 198°. The following derivatives of N-*methyl*-γ-*methylenedihydropyridine* (from γ-picoline methiodide) are described: *phenylthiocarbimide*, brown leaflets, m. p. 218°; *phenylcarbimide*, yellow needles, m. p. 196°. The *pseudo*-bases from pyridine methiodide and from β-picoline methiodide gave no recognisable crystalline products with either phenylcarbimide or thiocarbimide. N-*Methyl*-α-*methylenedihydroquinoline* with carbon disulphide gave no definite product but the following are described: *phenylthiocarbimide*, coppery leaflets, m. p. 170°; *hydriodide*, pale yellow, m. p. 192°; *perchlorate*, yellowish-brown, m. p. 188—190°; *picrate*, yellow, m. p. 168—169°; *phenylcarbimide*, yellow crystals, m. p. 173°; *hydriodide*, yellow, m. p. 190—191°; *perchlorate*, colourless, m. p. 199°; *picrate*, m. p. 168—169°. Derivatives of N-*ethyl*-α-*methylenedihydroquinoline* are: *phenylthiocarbimide*, reddish-brown crystals, m. p. 162°; *phenylcarbimide*, yellow needles, m. p. 167°. Derivatives of *methylene-anhydro base from* α : γ-*dimethylquinoline ethiodide* are: *phenylthiocarbimide*, reddish-brown needles, m. p. 145°; *phenylcarbimide*, yellow needles, m. p. 207°. Crystalline *additive* compounds were also obtained from the base derived from lepidine ethiodide, but were not examined further. Experiments were carried out also with the *pseudo*-bases derived from 2-ethylquinoline ethiodide, 4-ethylquinoline ethiodide, α-*iso*propylquinoline ethiodide, and quinoline ethiodide itself, but no crystalline additive compounds could be obtained.

F. A. M.

Arylated Pyridines. IV. *N*-Alkylquinopyridanes. W. DILTHEY, C. AMMON, and A. EBERT (*J. pr. Chem.*, 1924, [ii], **107**, 7—15; cf. A., 1921, i, 735; 1922, i, 272).—The arylated quinopyridanes obtained by the action of ammonia on the *N*-arylpyridinium salts formed from primary amines and *p*-hydroxylarylpyrylium salts are considered to possess a quinoid structure in the yellowish-red anhydro bases and a benzenoid structure in their bright yellow salts and hydrates. The additive compounds of the bases with benzene are also assigned a quinoid structure. The following individual compounds are described: 1 : 2 : 6-*triphenyl*-4-p-*hydroxyphenylpyridinium chloride*, $C_{29}H_{22}ONCl,0{\cdot}5HCl$, bright yellow crystals, m. p. 335°, was obtained from 2 : 6-diphenyl-4-*p*-hydroxyphenylpyrylium chloride and aniline (cf. A., 1922, i, 272), and on heating in a xylene bath this gives the dark yellow, neutral *chloride*, $C_{29}H_{22}ONCl$. The two chlorides behave very differently with alcoholic ammonia. The hydrochloride yields a very stable meriquinoid *salt*, $C_{58}H_{43}O_2N_2Cl$, m. p. about 295—300°, from which chlorine is removed quantitatively only by boiling with silver hydroxide. The neutral chloride, in the same way, is converted into a *dihydrate* of the anhydro base, 1 : 2 : 6-*triphenyl*-4-*quino*-1 : 4-*dihydropyridine*. The dihydrate, yellow plates, darkens at 120—130°, melting twice between this temperature and 263°. When dehydrated, the dihydrate affords the orange monohydrate, from which the dark red anhydro base (yellow *picrate* and *nitrate*) is obtained, this, when heated, behaving similarly to the dihydrate, melting first at 175° and then, after solidifying, at 263° to a dark red fluid. With benzene, an *additive* compound, $C_{29}H_{21}ON,C_6H_6$ is formed, as fine, red needles, these, on heating at 110°, giving the anhydro base. Similarly, 2 : 6-diphenyl-4-*p*-hydroxyphenylpyrylium chloride, on heating with *p*-toluidine, gives 2 : 6-*diphenyl*-4-p-*hydroxyphenyl*-1-p-*tolylpyridinium chloride*, bright yellow plates ($+2H_2O$; the water is lost at 100—130°, giving the anhydrous compound, m. p. 343—345°). The *nitrate* is yellow, m. p. 168° (decomp.). With alcoholic ammonia, the chloride yields a *dihydrate* of the anhydro base, yellowish-red needles, which lose their water at 100—130°, giving the anhydro base, 2 : 6-*diphenyl*-1-p-*tolyl*-4-*quino*-1 : 4-*dihydropyridine*, reddish-violet, m. p. 293°. The anhydro base forms an insoluble *additive* compound with benzene, $C_{30}H_{23}ON,C_6H_6$.

From the reaction product of 4 : 6-diphenyl-2-*p*-hydroxyphenylpyrylium iodide and β-naphthylamine in benzene solution, the *picrate*, yellow, m. p. 162—163°, and *perchlorate*, yellow, m. p. 177—178°, of 4 : 6-diphenyl-2-*p*-hydroxyphenyl-1-β-naphthylpyridine were isolated. R. B.

5 : 6 : 7 : 8-Tetrahydroquinolines and their Derivatives. IV. J. VON BRAUN, W. GMELIN, and A. PETZOLD (*Ber.*, 1924, **57**, [*B*], 382—391; cf. von Braun, Gmelin, and Schultheiss, A., 1923, i, 835).—Further examples are cited which confirm the previous conclusion that the presence of alkyl substituents, according to their number and weight, in the pyridine half of the quinoline molecule inhibits to a greater or less extent the introduction of

hydrogen atoms in the presence of nickel into the 1 : 2 : 3 : 4-positions and favours the production of 5 : 6 : 7 : 8-derivatives. The maximum effect is observed in the case of 2 : 3 : 4-trimethylquinoline, which, in complete contrast to quinoline itself, is hydrogenated exclusively in the benzenoid nucleus. The introduction of alkyl groups into the 5 : 6 : 7 : 8-positions exerts an opposite effect. The observations are explained by the hypothesis that the quinoline derivatives are equilibrium mixtures of two forms (benzenoid and centric structures alternating in each nucleus); in extreme cases of loading with substituents, only one variety is present.

2-Propylquinoline dissolved in decahydronaphthalene is converted by hydrogen in the presence of nickel at 170° into a mixture of 2-*propyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (65%) and 2-*propyl*-5 : 6 : 7 : 8-*tetrahydroquinoline* (35%). The former compound is a colourless liquid, b. p. 140—141°/10 mm. (*hydrochloride*, m. p. 221°; *benzoyl* derivative, microscopic crystals, m. p. 101°), whereas the latter base is a colourless liquid with a pronounced odour of pyridine, b. p. 130—132°/11 mm. (the non-crystalline *hydrochloride*, the *chloroplatinate*, decomp. 62°, and the *picrate*, yellow needles, m. p. 119°, are described). 2-*Propyldecahydroquinoline*, obtained in almost quantitative yield by the reduction of 2-propyl-5 : 6 : 7 : 8-tetrahydroquinoline with sodium and alcohol, has b. p. 123—125°/20 mm.; it somewhat resembles coniine in physiological activity. It yields a non-crystalline *nitroso* derivative, an extremely hygroscopic *hydrochloride*, and a *picrate*, m. p. 134—135°.

4-Phenyl-2-methylquinoline gives 4-phenyl-2-methyl-1 : 2 : 3 : 4-tetrahydroquinoline, m. p. 66—67° (16%), and 4-*phenyl*-2-*methyl*-5 : 6 : 7 : 8-*tetrahydroquinoline*, a viscous liquid, b. p. 181—183°/13 mm. (84%). The latter compound yields a *picrate*, m. p. 186—187°, a non-crystalline *hydrochloride*, and a yellow *chloroplatinate*, decomp. 145—147°.

2 : 3 : 4-Trimethylquinoline, m. p. 92° (65° is recorded in the literature), is prepared in the usual manner from aniline and methylacetylacetone; the *picrate*, m. p. 216°, *hydrochloride*, m. p. 274°, and lemon-yellow *methiodide*, m. p. 260°, are described. When hydrogenated in the presence of nickel at 155—160°, the base yields about 2% of 2 : 3 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydroquinoline, which is identified as the *chloroplatinate* of the corresponding *methochloride*, $C_{25}N_{41}Cl_2N_6Pt$, lustrous, orange-coloured needles, m. p. 176°. The main product of the reduction is 2 : 3 : 4-*trimethyl*-5 : 6 : 7 : 8-*tetrahydroquinoline*, a liquid with an odour resembling that of pyridine, b. p. 145—147°/13 mm., which yields a crystalline *dihydrate*, m. p. 31—32°; the *picrate*, m. p. 147°, *hydrochloride*, m. p. 174°, and *methiodide*, m. p. 125—126°, are described. The base is reduced by sodium and alcohol to 2 : 3 : 4-*trimethyldecahydroquinoline*, a colourless liquid with a pronounced odour of hemlock, b. p. 115°/13 mm.; the non-crystalline *nitroso* derivative, the *hydrochloride*, and the *product*, $C_{14}H_{28}NI$ (obtained by exhaustive methylation), a crystalline powder, m. p. 227° after softening at 218°, are described.

2 : 6-Dimethylquinoline readily undergoes catalytic hydrogenation at 105°, yielding 2 : 6-dimethyl-5 : 6 : 7 : 8-tetrahydroquinoline (1·5%) (*picrate*, m. p. 127°; *chloroplatinate*, $C_{22}H_{32}N_2Cl_6Pt$, an orange-coloured powder, decomp. 185°), and 2 : 6-dimethyl-1 : 3 : 2 : 4-tetrahydroquinoline (98·5%), b. p. 133°/12 mm., m. p. 32° (*benzoyl* derivative), m. p. 103°.

Acetylacetone and *p*-xylidine readily yield the corresponding *xylidide*, $C_{13}H_{17}ON$, b. p. about 170°/12 mm., m. p. 41°, which with concentrated sulphuric acid gives 2 : 4 : 5 : 8-*tetramethylquinoline*, a pale yellow, crystalline mass, m. p. 48°, b. p. 168—172°/12 mm.; the base exhibits a pronounced, bluish-violet fluorescence in acid solution. The *hydrochloride*, m. p. 254° after sintering at 243°, and the *picrate*, small needles, m. p. 161°, are described; the methiodide could not be obtained. The base is hydrogenated at 160—170° to a mixture of 2 : 4 : 5 : 8-*tetramethyl*-5 : 6 : 7 : 8-*tetrahydroquinoline* (4%), a colourless liquid, b. p. 135—137°/12 mm. (the non-crystalline *hydrochloride*, the *chloroplatinate*, coarse crystals which blacken above 196°, and the *picrate*, m. p. 131°, are described), and 2 : 4 : 5 : 8-*tetramethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (96%), b. p. 143—145°/12 mm. (the non-crystalline *benzoyl* derivative, the *hydrochloride*, m. p. 211°, and the *picrate*, m. p. 160°, are described).

[With K. MÜNCKER.]—Tetrahydro-α-naphthylamine reacts readily with acetylacetone to yield the *compound* $C_{10}H_{11}N{:}CMe{\cdot}CH_2{\cdot}Ac$, a viscous liquid, b. p. 208°/15 mm., which with concentrated sulphuric acid gives 2 : 4-*dimethyl*-7 : 8 : 9 : 10-*tetrahydro*-α-*naphthaquinoline*, b. p. 196—200°/15 mm., m. p. 49° (*hydrochloride*, m. p. 243°; *picrate*, m. p. 201°; *methiodide*, m. p. 254°). The catalytic hydrogenation of the base proceeds with unusual difficulty; even at temperatures above 200° the action stops prematurely, owing to poisoning of the catalyst. The main product is 2 : 4-*dimethyl*-1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*octahydro*-α-*naphthaquinoline*, a viscous liquid, b. p. 190°/16 mm. (*benzoyl* derivative, m. p. 130—131°; *nitroso* compound, m. p. 62°; *hydrochloride*, m. p. 204°; *picrate*, m. p. 130°). The portion of the product which does not react with benzoyl chloride appears to have suffered partial hydrogenation in the central nucleus. The catalytic reduction of 2 : 4-dimethyl-α-naphthaquinoline, m. p. 52°, yields a mixture of unchanged base, 2 : 4-dimethyl-7 : 8 : 9 : 10-tetrahydro-α-naphthaquinoline, and the above octahydro base; the primary change occurs at the extreme benzene nucleus. H. W.

Intramolecular Condensation Reactions of Aminoacetals and Aminoaldehydes. I. Synthesis of Dihydroquinoline and certain Homologues. C. RÄTH (*Ber.*, 1924, **57**, [*B*], 550—555).—If chloro- or bromo-acetal is heated with *o*-toluidine in a closed tube at 260°, 1 : 2-*dihydroquinoline* (90% yield) is obtained as an almost colourless liquid, b. p. 226° (*hydrochloride*, white, crystalline powder, m. p. 214°; *picrate*, yellow, crystalline powder, m. p. 199—200°; *nitroso* derivative, a viscous, yellow oil), and is accompanied by small quantities of the intermediately formed

o-toluidine-N-monoacetal, a viscous substance, b. p. 250—262°. On heating 1 : 2-dihydroquinoline with ethylene chlorohydrin in benzene solution, 1-(β-*hydroxyethyl*)-1 : 2-*dihydroquinoline* is formed as a viscous, pinkish liquid, b. p. 166—168°/11 mm. The *hydrochloride*, *picrate*, and *methiodide* were obtained only as oils.

In a similar way, β-bromopropionacetal condenses with *o*-toluidine to form 1 : 2-*dihydroquinaldine*, which is a faintly yellow liquid (b. p. 234—240°) affording an oily *nitroso* derivative; the *hydrochloride*, a white, crystalline powder, has m. p. 197—198°; the *picrate*, yellow crystals, m. p. 189—190°. If methyl-*o*-toluidine be used in place of *o*-toluidine, the product is 1-methyl-1 : 2-dihydroquinaldine, b. p. 252—260° (Freund, A., 1906, i, 600; 1909, i, 417); the *hydrochloride* is an oil, the *picrate* yellow rosettes, m. p. 148—150°. As a by-product was obtained α-*o-tolylmethylaminopropaldehyde*, $CH_3 \cdot C_6H_4 \cdot NMe \cdot CHMe \cdot CHO$, b. p. 283—288°, which forms a *picrate*, m. p. 152—153°. F. A. M.

The Reactivity of the Chlorine Atom in the 2-Position in Quinoline and Quinoline Derivatives. J. Tröger and H. Meinecke (*J. pr. Chem.*, 1923, [ii], **106**, 203—225).—2-Chloroquinoline reacts slowly with sodium benzenesulphinate in presence of alcohol to give 2-*benzenesulphonylquinoline*, colourless needles, m. p. 160°. This compound is unaffected by a short fusion with alkali, prolonged fusion effecting profound decomposition. When heated with dilute hydrochloric acid at 235°, it affords carbostyril, benzenesulphinic acid, and benzene disulphoxide. It forms no double salts. 2-Chloroquinoline does not react with alkali derivatives of thiophenols, but 2-chloro-3-benzenesulphonylquinoline and the sodium derivative of *p*-thioltoluene afford 3-*benzenesulphonylcarbostyril* p-*tolyl thioether*, $C_9H_5N(SO_2Ph)(SC_7H_7)$, colourless needles, m. p. 131° with previous sintering. When 2-chloro-3-benzenesulphonylquinoline is heated in alcoholic solution with sodium benzenesulphinate at 130°, 2 : 3-dibenzenesulphonylquinoline (m. p. 204°) results (cf. A., 1923, i, 368).

2-o-*Toluenesulphonylquinoline* (colourless prisms, m. p. 127°) was prepared by the above method. 2-*Amino*-3-o-*toluenesulphonylquinoline* (from *o*-toluenesulphonylacetonitrile and *o*-aminobenzaldehyde), white prisms, m. p. 179·5° (*hydrochloride*, $C_{16}H_{14}O_2N_2S,HCl,H_2O$, white crystals), is converted by nitrous acid into 3-o-*toluenesulphonylcarbostyril*, yellow prisms, m. p. 270°, this substance, with phosphorus pentachloride, affording 2-*chloro*-3-o-*toluenesulphonylquinoline*, colourless needles, m. p. 161°.

From the last-named chloro compound, 3-o-*toluenesulphonylcarbostyril* p-*tolyl thioether* (white crystals, m. p. 191°), 3-o-*toluenesulphonyl*-2-*benzenesulphonylquinoline* (colourless prisms, m. p. 260°), and 3-o-*toluenesulphonylcarbostyril phenyl thioether* (colourless needles, m. p. 154°) were obtained. The last-named ether, on oxidation, affords 3-*o*-toluenesulphonylcarbostyril.

Sodium *p*-toluenesulphinate reacts less rapidly than the benzenesulphinate with 2-chloroquinoline, 2-p-*toluenesulphonylquinoline*

(white crystals, m. p. 141°) resulting. Other compounds in this series are: 3-p-*toluenesulphonylcarbostyril* p-*tolyl thioether*, colourless crystals, m. p. 195°; 3-p-*toluenesulphonyl*-2-p-*toluenesulphonylquinoline*, colourless needles, m. p. 184—185°; and 3-p-*toluenesulphonylthiocarbostyril*, lemon-yellow powder, m. p. 226°.

2-p-*Chlorobenzenesulphonylquinoline* forms white needles, m. p. 190°; 3-p-*chlorobenzenesulphonylcarbostyril phenyl thioether* (yellow needles, m. p. 149°) is formed together with some 3-*p*-chlorobenzenesulphonylcarbostyril when 2-chloro-3-*p*-chlorobenzenesulphonylquinoline reacts with sodium thiophenoxide, and on oxidation affords 3-p-*chlorobenzenesulphonyl*-2-*benzenesulphonylquinoline*, white crystals, m. p. 264° (sintering at 250°).

3-p-*Chlorobenzenesulphonylcarbostyril* p-*tolyl thioether*, colourless needles, m. p. 147°, cannot be oxidised to the corresponding disulphone. 2-p-*Bromobenzenesulphonylquinoline* forms white needles, m. p. 145°. 2-*Amino*-3-p-*bromobenzenesulphonylquinoline*, lemon-yellow needles, m. p. 223°, forms a *hydrochloride*, needles, m. p. 256° (decomp.), *nitrate*, yellow, crystalline powder, m. p. (indef.) 105—224°, and *chloroplatinate*, yellowish-red crystals, and is converted by nitrous acid into 3-p-*bromobenzenesulphonylcarbostyril*, yellow needles, m. p. 269°. The last-named substance is converted by phosphorus pentachloride into 2-*chloro*-3-p-*bromobenzenesulphonylquinoline*, colourless needles, m. p. 181·5°. The following were also prepared: 3-p-*bromobenzenesulphonylcarbostyril ethyl ether*, colourless needles, m. p. 156°; 3-p-*bromobenzenesulphonylthiocarbostyril*, yellow crystals, m. p. 254°, and 3-p-*bromobenzenesulphonylcarbostyril* p-*tolyl thioether*, white needles, m. p. 159°.

2-β-*Naphthalenesulphonylquinoline* forms colourless stars, m. p. 137°. 2-*Amino*-3-β-*naphthalenesulphonylquinoline*, yellow needles, has m. p. 180° and forms a *hydrochloride*, yellow needles, m. p. 250° (with previous decomp.), and a *nitrate*, white needles. 3-β-*Naphthalenesulphonylcarbostyril* forms yellow needles, m. p. 294°; 2-*chloro*-3-β-*naphthalenesulphonylquinoline*, yellow crystals, has m. p. 159°; 3-β-*naphthalenesulphonylcarbostyril ethyl ether* forms yellow needles, m. p. 121°; 3-β-*naphthalenesulphonylcarbostyril* p-*tolyl thioether*, silver crystals, has m. p. 176° and oxidises irregularly.

2-o-*Anisolesulphonylquinoline* forms rhombs, m. p. 134°. 2-*Amino*-3-o-*anisolesulphonylquinoline*, colourless crystals, has m. p. 239°, and was converted into 3-o-*anisolesulphonylcarbostyril*, yellow crystals, m. p. 250°. 2-*Chloro*-3-o-*anisolesulphonylquinoline*, quadratic crystals, m. p. 171°, was converted into 3-o-*anisolesulphonylcarbostyril phenyl thioether*, colourless rhombohedra, m. p. 160°, and into 3-o-*anisolesulphonylthiocarbostyril*, yellow crystals, m. p. 233° (*methyl* ether, colourless crystals, m. p. 150°).

2-p-*Phenetolesulphonylquinoline*, white leaflets, has m. p. 133·5°. 2-*Amino*-3-p-*phenetolesulphonylquinoline* forms yellow leaflets, m. p. 178° [*hydrochloride*, needles, m. p. 233° (decomp.)], and was converted into 3-p-*phenetolesulphonylcarbostyril*, yellow needles, m. p. 241°. 2-*Chloro*-3-p-*phenetolesulphonylquinoline*, yellow crystals, m. p. 162°, was converted into 3-p-*phenetolesulphonylcarbostyril* p-*tolyl thioether*, colourless needles, m. p. 141°, the last-named substance

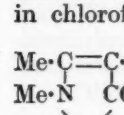
affording, on oxidation, 3-p-*phenetolesulphonyl*-2-p-*toluenesulphonylquinoline*, needles, m. p. 249° (sintering at 239°). 3-p-*Phenetolesulphonylthiocarbostyril*, yellow needles, has m. p. 142°.

From the above it is seen that in 2-chloroquinoline, the chlorine atom cannot be displaced by the ·SR radical, whereas the presence of the grouping ·SO_2R in position 3 (especially if R is a *p*-tolyl radical) facilitates the displacement. Again, whilst 2-amino-β-arylsulphonylquinolines (monoacidic bases) cannot be diazotised, the amino radical can readily be displaced by hydroxyl, using nitrous acid. E. E. T.

Carbithionic and Thionic Acid Derivatives of Pyrazolones. E. BENARY and A. SCHMIDT (*Ber.*, 1924, **57**, [*B*], 517—522).—By the action of chlorocarbonic ester, or ethyl bromide, on antipyrine in carbon disulphide solution, a product is obtained according to the equation:

$$C_{11}H_{11}ON_2+EtBr+CS_2=C_{11}H_{11}ON_2\cdot CS\cdot SEt+HBr.$$

Since the new substance does not give the typical nitroso reaction of antipyrine, it is assumed that the group –CS·SEt has occupied position 4 and that the substance is *ethyl* 1-*phenyl*-2 : 3-*dimethylpyrazolone*-5-*carbithionate* (cf. Houben, A., 1906, i, 847). It forms orange leaflets, m. p. 178·5—179°, gives no nitroso compound with nitrous acid, and forms an intense red precipitate with bromine in chloroform solution. When treated with alcoholic potassium hydroxide, it affords ethyl mercaptan and 1-*phenyl*-2 : 3-*dimethylpyrazolone*-5-*thionic acid*, sulphur-yellow needles, m. p. 81—82° (annexed formula) (*potassium* and *silver* salts described). The *methyl* ester, yellow needles (+1·5H_2O) has m. p. 95° (anhydrous ester, m. p. 113—114°). The following were made in a similar manner from the appropriate substance, ethyl bromide, and aluminium chloride in carbon disulphide solution.



Ethyl 1-*phenyl*-3-*methyl*-5-*pyrazolone*-4-*carbithionate*, from 1-methyl-3-phenyl-5-pyrazolone, forms greenish-yellow prisms, m. p. 81—82°. *Ethyl* 3-*methyl*-5-*pyrazolone*-4-*carbithionate*, orange prisms or needles, m. p. 186°, which with alkali yields 3-methyl-5-pyrazolone; on treating the alkaline solution from the hydrolysis with methyl sulphate, white or pale yellow needles (m. p. 115·5°) are formed, of *methyl* 1 : 2 : 3-(or 1 : 2 : 5-)*trimethyl*-5-*pyrazolone*-4-*carbithionate*. *Ethyl* 5-*pyrazolone*-4-*carbithionate*, from 5-pyrazolone, forms reddish-brown prisms, m. p. 184—185°. *Ethyl* 1-*phenyl*-5-*methyl*-3-*pyrazolone*-4-*carbithionate* forms orange-yellow leaflets, m. p. 114°. From thiopyrine a yellow, crystalline *substance*, m. p. 166°, probably the corresponding carbithionic acid, was obtained. F. A. M.

Dipyridyls from Pyridine. C. R. SMITH (*J. Amer. Chem. Soc.*, 1924, **46**, 414—419).—The author describes the preparation and separation of 2 : 2-, 3 : 3-, 3 : 4-, and 4 : 4-dipyridyls. 3 : 4-*Dipyridyl* (plates, m. p. 61°, b. p. 297°) forms a *dihydrochloride*,

mercurichloride, and *chloroplatinate* and is distinguished from its isomerides by certain colour reactions. On oxidation with potassium permanganate, it affords nicotinic and *iso*nicotinic acids. In the interaction of sodium and pyridine in presence of dry oxygen, the proportions of the various isomerides produced depend on the time, temperature, and pressure conditions. A. B. S.

The Constitution of the Products arising from the Condensation of *o*-Aminoazo Compounds with Aldehydes. II. OTTO FISCHER (*J. pr. Chem.*, 1924, [ii], **107**, 16—49; cf. A., 1922, i, 956).—A further series of *N*-substituted iminazoles, some already known, has been obtained by the condensation of *o*-aminoazo compounds with aldehydes, and the reduction of these with hydriodic acid is described, the products being a benziminazole and an amine. The condensation products of chrysoidine and aldehydes are shown to be derivatives of 1-anilino-2-phenyl-5-aminobenziminazole. The action of benzyl chloride on *o*-aminoazo compounds did not give the expected *N*-aryldihydrobenziminazoles, but their decomposition products, *e.g.*, aniline and 2-phenylnaphthiminazole. If the benzyl group is introduced into the amine prior to coupling, the azo dyes formed easily decompose in a similar way.

[With E. THIEL.]—From benzeneazo-β-naphthylamine, the following compounds have been prepared. With acetaldehyde, 1-anilino-2-methylnaphthiminazole [yellow *picrate*, m. p. 234°; yellow *nitrosoamine*, decomp. 124°; *acetyl* compound, m. p. 230° (decomp.)]. With methyl iodide in benzene solution it gives a *methyl* base, lustrous, colourless plates, m. p. 195° (*hydrochloride*, m. p. 250°), which does not form a nitrosoamine. With *o*-chlorbenzaldehyde, 1-*anilino*-2-o-*chlorphenylnaphthiminazole*, colourless, tufted needles, m. p. 231° [*picrate*, m. p. 192° (decomp.)]. With salicylaldehyde, 1-*o*-hydroxyanilino-2-phenylnaphthiminazole [golden-yellow *nitrosoamine*, *diacetyl* compound, m. p. 169°(decomp.)], an intermediate compound, violet-tinged needles, $C_{23}H_{17}ON_3$, being isolated which goes over into the colourless iminazole at 100—110°. With *p*-hydroxybenzaldehyde, 1-*anilino*-2-p-*hydroxyphenylnaphthiminazole*, colourless crystals, m. p. 233° (decomp.) (*nitrosoamine*, decomp. 200°, *diacetyl* compound, prisms, m. p. 224°).

[With F. STAUBER and W. HILD.]—When heated with hydriodic acid (*d* 1·7) under pressure, the *N*-arylbenziminazoles and naphthiminazoles are converted into the corresponding primary amine and iminazole. The iminazoles are not further decomposed even at 180—200°. The following compounds have been prepared.

From *o*-aminoazo-*p*-toluene and benzaldehyde, 1-*p*-toluidino-2-phenyl-5-methylbenziminazole, which on reduction yields *p*-toluidine and 2-*phenyl*-5-*methylbenziminazole*, dense white crystals, m. p. 240°. Similarly, *o*-chlorobenzaldehyde yields 1-p-*toluidino*-2-o-*chlorophenyl*-5-*methylbenziminazole*, white, monoclinic needles, m. p. 195° (*picrate*, m. p. 178—179°, *nitrosoamine*, decomp. 124°), which is reduced to *p*-toluidine and 2-o-*chlorophenyl*-5-*methylbenziminazole*, white needles, m. p. 160° (*picrate*, decomp. 189°). From *m*-nitrobenzaldehyde is similarly obtained 1-*p*-toluidino-2-*m*-nitrophenyl-5-

methylbenziminazole, greyish-yellow needles, decomp. 224—225° (*picrate*, decomp. 174°; *nitrosoamine*, decomp. 120°), and on reduction, *p*-toluidine and 2-m-*aminophenyl-5-methylbenziminazole*, white, crystalline plates, m. p. 236°. With *o*-nitrobenzaldehyde, 1-*p*-toluidino-2-*o*-nitrophenyl-5-methylbenziminazole (*picrate*, decomp. 182°; *nitrosoamine*, decomp. 130°) and 2-o-*aminophenyl-5-methylbenziminazole*, white needles, m. p. 190°; and with *p*-nitrobenzaldehyde, 1-*p*-toluidino-2-*p*-nitrophenyl-5-methylbenziminazole and 2-p-*aminophenyl-5-methylbenziminazole*, white plates, m. p. 124°, containing water of crystallisation. This base, when diazotised and coupled with β-naphthol in alcohol–pyridine solution, gives a reddish-brown azo dye, m. p. 330°. From *o*-aminoazo-*p*-toluene and *p*-dimethylaminobenzaldehyde, 1-p-*toluidino*-2-*dimethylaminophenyl-5-methylbenziminazole*, white needles, m. p. 249° (*picrate*, m. p. 177°; *nitrosoamine*, decomp. 85°), is obtained, which on reduction yields *p*-toluidine and the iminazole, m. p. 124°, obtained in the reduction of the base from *p*-nitrobenzaldehyde.

Benzeneazo-β-naphthylamine and benzaldehyde yield 1-anilino-2-phenylnaphthiminazole, which on reduction yields 2-phenylnaphthiminazole, m. p. 217—218°. The reduction of the condensation products of substituted benzaldehydes and benzeneazo-β-naphthylamine yields the same phenylnaphthiminazole. From *p*-hydroxybenzeneazo-β-naphthylamine (*diacetyl* derivative, m. p. 184°, *dibenzoyl* derivative, m. p. 199°) the following compounds were obtained: with benzaldehyde in alcoholic solution, 1-p-*hydroxyanilino*-2-*phenylnaphthiminazole*, white needles, m. p. 183° (*nitrosoamine*, decomp. 135°), which on reduction yields *p*-aminophenol and 2-phenylnaphthiminazole; with *o*-chlorobenzaldehyde, 1-p-*hydroxyanilino*-2-o-*chlorophenylnaphthiminazole*, white needles, m. p. 198° (*nitrosoamine*, decomp. 110°), and on reduction *p*-aminophenol and 2-o-*chlorophenylnaphthiminazole*, white needles, m. p. 214°; with salicylaldehyde in methyl-alcoholic solution, 1-p-*hydroxyanilino*-2-o-*hydroxyphenylnaphthiminazole*, white needles, m. p. 276°, which on reduction yields 2-o-*hydroxyphenylnaphthiminazole*, white needles, m. p. 280°; with furfuraldehyde, 1-p-*hydroxyanilino*-2-*furylnaphthiminazole*, white needles, m. p. 195° (*picrate*, yellow powder, *nitrosoamine*, yellow, easily decomp.). In contrast to the foregoing substituted iminazoles, which are very stable to most reducing agents, 1-p-*nitroanilino*-2-o-*chlorophenylnaphthiminazole*, bright yellow crystals, m. p. 283° (*nitrosoamine*, decomp. 105—107°), prepared from *p*-nitroanilinoazo-β-naphthylamine and *o*-chlorobenzaldehyde in acetic acid solution, yields *p*-phenylenediamine and 2-*o*-chlorophenylnaphthiminazole on reduction with zinc and acetic acid.

[With G. Seufert and H. Hojer.]—The azo dye obtained from diazotised anthranilic acid and β-naphthylamine forms crimson-red needles, m. p. 182—183°; it gives, with benzaldehyde, 1-o-*carboxyanilino*-2-*phenylnaphthiminazole*, colourless, monoclinic prisms, m. p. 263—264°, decomp., which on nitration in acetic acid yields 1-o-*carboxy*-p-*nitroanilino*-2-*phenylnaphthiminazole*, bright yellow pyramids, m. p. 274°, and this on reduction with hydriodic acid gives

2-phenylnaphthiminazole. With acetaldehyde, the same dye yields 1-o-*carboxyanilino*-2-*methylnaphthiminazole*, colourless, monoclinic plates, m. p. 283° (after slight decomp. at 260°), which gives 2-methylnaphthiminazole, m. p. 168° (*picrate*, m. p. 242°), on reduction.

1-m-*Carboxybenzeneazo*-β-*naphthylamine*, yellowish-red needles, m. p. 220°, gives condensation products with aldehydes which are distinguished by their insolubility in solvents. The following compounds were prepared. From acetaldehyde, 1-m-*carboxyanilino*-2-*methylnaphthiminazole*, white, crystalline powder, m. p. 276°; from furfuraldehyde, 1-m-*carboxyanilino*-2-*furylnaphthiminazole*, m. p. 273—274°; from salicylaldehyde, 1-m-*carboxyanilino*-2-o-*hydroxyphenylnaphthiminazole*, colourless granules, m. p. 232° (*nitrosoamine*, decomp. 110°).

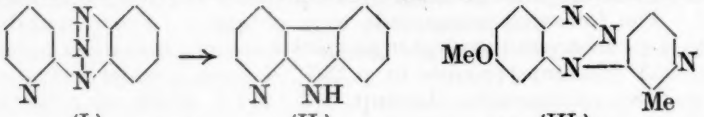
p-Carboxybenzeneazo-β-naphthylamine crystallises from benzene–alcohol in crimson-red needles, m. p. 263—264°; it condenses with aldehydes in alcoholic solution in the presence of pyridine or acetic acid. The following compounds were obtained. From benzaldehyde, 1-p-*carboxyanilino*-2-*phenylnaphthiminazole*, colourless prisms, m. p. 255° (decomp.) [*picrate*, m. p. 205° (decomp.), *acetyl* derivative, m. p. 218°, *nitrosoamine*, decomp. 213—214°], which on reduction yields 2-phenylnaphthiminazole and *p*-aminobenzoic acid. On nitration, the original base gives 1(2 : 4-*dinitroanilino*)-2-*phenylnaphthiminazole*, small, yellow plates, decomp. 270—272°. The dinitro compound with hydriodic acid gives 2-phenylnaphthiminazole and 1 : 2 : 4-triaminobenzene. With acetaldehyde, the azo dye gives 1-p-*carboxyanilino*-2-*methylnaphthiminazole*, white plates, m. p. 287° (*dinitro* derivative, m. p. 235°, yielding 2-methylnaphthiminazole on reduction). With furfuraldehyde, 1-p-*carboxyanilino*-2-*furylnaphthiminazole*, colourless prisms, m. p. 251° (greenish-yellow *nitrosoamine*).

[With F. VON MANN-SIECHLER.]—The base, $C_{19}H_{16}N_4$, colourless, white plates, m. p. 228°, obtained by the action of benzaldehyde on chrysoidine (cf. A., 1898, i, 155) gives a *diacetyl* derivative, m. p. 105° (decomp.), a *picrate*, decomp. 204°, a *picrolonate*, decomp. 186°, and with aldehydes stable, well-crystallised benzylidene derivatives, which can be prepared directly from chrysoidine and aldehyde (2 mols.). Thus benzaldehyde and chrysoidine afford the compound $C_{26}M_{20}N_4$, bright yellow plates, m. p. 242° (*nitrosoamine*, decomp. 110°), which with 10% sulphuric acid affords benzaldehyde and 1-anilino-2-phenylaminobenziminazole, white flocks, m. p. 229°. Similarly, chrysoidine and salicylaldehyde give the compound $C_{26}H_{20}O_2N_4$, bright yellow plates, m. p. 242° (*nitrosoamine*, decomp. 125°), from which dilute sulphuric acid splits off 1 mol. of salicylaldehyde. By diazotisation in alcoholic solution and treatment with 95% alcohol, the base $C_{19}H_{16}N_4$ was converted into 1-*anilino*-2-*phenylbenziminazole*, snow-white prisms, m. p. 211° (*picrate*, decomp. 199°; *picronolate*, decomp. 220°; *nitrosoamine*, decomp. 137°), and this on reduction with hydriodic acid gives the known 2-phenylbenziminazole.

[With F. ELFLEIN and K. MÜLLER.]—The action of benzyl chloride on benzeneazo-β-naphthylamine, either alone or in acetic acid solu-

tion, gives aniline and 2-phenylnaphthiminazole. Similar results were obtained with *p*-tolueneazo-β-naphthylamine, *o*- and *m*-nitrobenzeneazo-β-naphthylamine, and *p*-anisoleazo-β-naphthylamine. Similarly, benzeneazo-β-benzylnaphthylamine (shining, light red needles, m. p. 136—138°), obtained by coupling benzyl-β-naphthylamine with benzene diazonium chloride in alcoholic solution, on boiling with alcoholic hydrochloric acid decomposes into aniline and 2-phenylnaphthiminazole. Similar results were obtained with *p*-tolueneazo-benzyl-β-naphthylamine and nitrobenzeneazo-benzyl-β-naphthylamine. R. B.

Harmine and Harmaline. VII. Synthesis of *apo*Harmine and of certain Carboline and Copyrine Derivatives. W. Lawson, W. H. Perkin, jun., and R. Robinson (*J. Chem. Soc.*, 1924, **125**, 626—657).—2-Chloropyridine and *o*-phenylenediamine condense to give *o*-aminophenyl-2-pyridylamine hydrochloride,



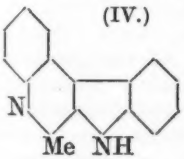
(I.) (II.) (III.)

which, when treated with nitrous acid, yields 1-α-*pyridylbenzotriazole* (I), colourless needles, m. p. 110—111°. The latter, when heated in small quantities with zinc chloride, gives 3-*carboline* (II), colourless needles, m. p. 210°; *hydrochloride*, needles from dilute hydrochloric acid; *mercurichloride*, needles; *hydrogen oxalate*, needles from dilute oxalic acid solution; *picrate*, canary-yellow needles, m. p. 260—264°. 2-Chloroquinoline and *o*-phenylenediamine similarly give 1-α-*quinolylbenzotriazole*, colourless prisms or needles, m. p. 145°, which, when heated, gives quinindoline, identical with that of Gabriel and Eschenbach (A., 1898, i, 199). The triazole (III) cannot be prepared by this method owing to the inactivity of β-halogen substituents in the pyridine molecule, and alternatively the preparation of 3-aminoquinaldine and 3-amino-2-methylpyridine was undertaken for condensation with the requisite halogen derivatives. 2-Methylquinoline-3 : 4-dicarboxylic acid (cf. Pfitzinger, A., 1898, i, 207), when strongly heated, gives the *anhydride*, colourless prisms, m. p. 218°, and when heated with carbamide at 230° gives the *imide*, pale yellow needles from ethyl acetate, m. p. 257°. The imide, when treated with bromine and potassium hydroxide, gives 3-*amino*-2-*methylquinoline*-4-*carboxylic acid*, pale yellow needles, m. p. 221—222° (decomp.), which, when heated at 225°, is smoothly converted into 3-amino-2-methylquinoline, m. p. 160—160·5°, identical with that prepared by Stark (A., 1907, i, 973). The condensation of this aminoquinaldine with various chlorobenzene derivatives could not be carried out, and is still under investigation.

Ethyl β-aminocrotonate and ethyl cinnamoylpyruvate condense to give *ethyl styrylmethylpyridinedicarboxylate*, which is isolated as a *picrate*, yellow needles, m. p. 147·5—148°. These, on treatment with ammonia and subsequent hydrolysis, give *styrylmethylpyridine*-

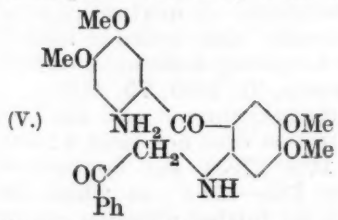
dicarboxylic acid, pale yellow prisms, m. p. 220—221°. This acid cannot be 4-styryl-2-methylpyridine-3 : 6-dicarboxylic acid, since, when boiled with aniline, it gives a *phenylimide*, which was isolated in two forms, (*a*), bright yellow needles, m. p. 228—230°, (*b*), yellow needles, m. p. 203—204°; *a* and *b* may be geometrical stereoisomerides, although *a* on recrystallisation from xylene gave *b*. The potassium salt of the dicarboxylic acid, on treatment with potassium permanganate, gives 2-*methylpyridine*-3 : 4 : 6-*tricarboxylic acid*, which was isolated as the *potassium barium* salt, colourless crystals, and also gives a *monopotassium* salt, colourless prisms, a characteristic *ferrous* salt, red or orange-brown prisms, and on treatment with an excess of aniline gives the *anilide phenylimide*, pale yellow needles, m. p. 237°, and also the *phenylimide* of 2-methylpyridine-3 : 4-dicarboxylic acid, colourless plates, m. p. 190°. The *tricarboxylic acid* itself crystallises from water in prisms $+3H_2O$, which, when anhydrous, darken at 219° and melt at 223° (decomp.), and was found not to be identical with the methylpyridinetricarboxylic acid obtained by Dobbie and Lauder (T., 1902, **81**, 154) from corydaline, the constitution of which is therefore still in doubt. The tricarboxylic acid in turn gives 2-methylpyridine-3 : 4-dicarboxylic acid, m. p. 252—256°. The synthesis of a substituted dibenzo*apo*harmine of the type (IV) was then undertaken in order that subsequent oxidation of the benzene nuclei should furnish *apo*harmine. Veratrone, the preparation of which from veratric acid has been greatly improved, was converted by nitric acid into 6 : 6′-*dinitro*-3 : 4 : 3′ : 4′-*tetramethoxybenzophenone* (dinitroveratrone), colourless needles from acetic acid, m. p. 225°, and the latter on reduction gives *diaminoveratrone*, yellow prisms, m. p. 210°. The 6 : 6′-position of the nitroxyl groups in dinitroveratrone is confirmed by converting diaminoveratrone into *diacetyldiaminoveratrone*, pale yellow needles, m. p. 203°, which, on treatment with nitric acid in acetic acid suspension, gives a theoretical yield of 6-nitroacetoveratrylamine (cf. Jones and Robinson, T., 1917, **111**, 914).

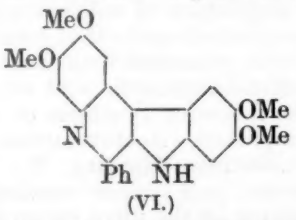
(IV.)



Diaminoveratrone, when heated with ω-bromoacetophenone in acetic acid, gives the hydrobromide of N-*phenacyldiaminoveratrone*, the *base* itself (V) forming greenish-yellow needles, m. p. 185—186° (decomp.). The base, when treated in alcoholic suspension with

(V.)





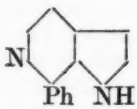
(VI.)

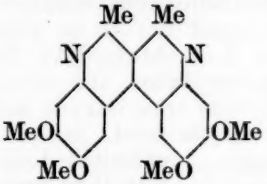
30% aqueous potassium hydroxide, gives *phenyldiveratroharmyrine* (phenyldiveratro-7-pyrindole) (VI), which crystallises from methyl alcohol +1 mol. of solvent, prisms, m. p. 145—148° (decomp.).

Replacement of the ω-bromoacetophenone by bromoacetone gave no compound analogous to *N*-phenacyldiaminoveratrone, but *methyldiveratroharmyrine* was obtained, colourless prisms, m. p. 254°, and gave a *methosulphate*, orange-yellow needles. The hydrobromide, on boiling with hydriodic acid, was completely demethylated, giving *methyltetrahydroxydibenzoharmyrine hydriodide*, yellow needles. Methyl- and phenyl-diveratroharmyrine were found on oxidation and subsequent treatment with alkali to give, however, only a minute yield of the corresponding *apo*harmine (VII), owing to almost complete destruction of the base by the oxidising agent.

2 : 7-Naphthyridine (copyrine) rings may be synthesised also from the 2 : 2-diaminobenzophenones. Thus diaminoveratrone condenses with acetylacetone to give *dimethyldiveratrocopyrine* (VIII), colourless needles from *n*-butyl alcohol, m. p. 230—231°,

(VII.)





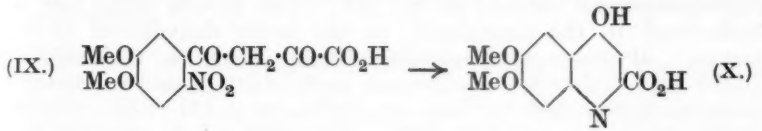
(VIII.)

forming a yellow, crystalline *nitrate*, and a *picrate* of composition $3C_{22}N_{22}O_4N_2{\cdot}5C_6H_3O_7N_3$, yellow needles, decomp. 245°. Diaminoveratrone with benzoylacetone gives similarly *phenylmethyldiveratrocopyrine*, colourless needles, m. p. 270°; with dibenzoylmethane gives *diphenyldiveratrocopyrine*, yellow needles, m. p. 362°, and with 1 : 3-diketohydrindene gives *o-phenylenediveratrocopyrine*, isolated as the *acetate*, yellow needles, the latter being converted by ammonia into the *base*, yellow needles, from nitrobenzene–*n*-butyl alcohol, m. p. 304°. Diaminoveratrone condenses also with ethyl acetoacetate to give *hydroxymethyldiveratrocopyrine*, pale yellow needles from quinoline, m. p. 320—330°; with ethyl malonate to give *dihydroxydiveratrocopyrine*, yellow needles from nitrobenzene, m. p. 300° (decomp.); with ethyl cyanoacetate to give *aminohydroxydiveratrocopyrine*, salmon-coloured needles from alcohol–nitrobenzene, decomp. 280°, chars 280—290°.

Xanthone (*oo'*-dichlorobenzophenone) can be prepared by the dry distillation of calcium *o*-chlorobenzoate. A mixture of ethyl benzoylacetate and ethyl β-aminocrotonate, when boiled in methyl-alcoholic potassium hydroxide, yields 6-hydroxy-4-phenyl-2-methylpyridine-3-carboxylic acid (cf. Ruhemann, T., 1899, **75**, 412).

The following synthesis of a dimethoxykynurenic acid has been accomplished. Acetoveratrone on nitration does not yield 4 : 5-dinitroveratrole (Harding, T., 1914, **105**, 2795), but 6-*nitroacetoveratrone*, pale yellow needles, m. p. 133—133·5°, in which the 6-position of the nitro group is shown by further nitration, giving 4 : 5-dinitroveratrole. 6-*Nitroacetoveratrone* condenses with anisaldehyde to give 6-*nitro*-3 : 4-*dimethoxyphenyl* 4-*methoxystyryl ketone*, pale yellow prisms from ethyl acetate, m. p. 170°, and also gives a

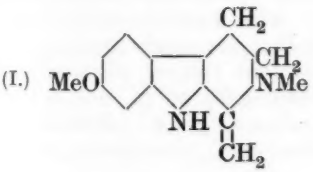
piperonylidene derivative, plates and needles, m. p. 176—177°, re-solidify and then re-melt above 200° (indef.). The 6-nitro compound on reduction gives 6-*aminoacetoveratrone*, colourless prisms, m. p. 133°, and when treated with sodium ethoxide and ethyl oxalate in alcohol yields 6-*nitroveratroylpyruvic acid* (IX), needles, m. p. 163°. The latter, when reduced with ferrous hydroxide,

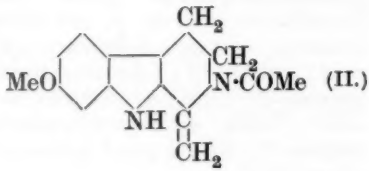


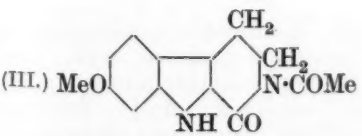
gives 4-*hydroxy*-6 : 7-*dimethoxyquinoline*-2-*carboxylic acid* (dimethoxykynurenic acid) (X), needles, sintering at 260°, m. p. 270° (decomp.). This acid when heated in glycerol solution loses carbon dioxide, giving 4-*hydroxy*-6 : 7-*dimethoxyquinoline*, colourless prisms, softening at 165—170°, re-solidifying and melting at 226°.

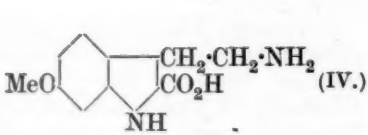
5 : 7-Dibromoisatin was converted into 5 : 7-dibromoisatinic acid, and the latter into 6 : 8-*dibromo*-2-*methylquinoline*-4-*carboxylic acid*, colourless needles, m. p. 267° (decomp.). The latter on heating gives 6 : 8-*dibromo*-2-*methylquinoline*, needles, m. p. 100°, *picrate*, orange-yellow needles, m. p. 155°. Attempts made to replace the bromine in the carboxylic acid by hydroxy groups and then by oxidation of the benzene nucleus to obtain 2-methylpyridine-4 : 5 : 6-tricarboxylic acid failed. F. G. M.

Harmine and Harmaline. VIII. Constitution of certain Harmaline Derivatives. H. Nishikawa, W. H. Perkin, jun., and R. Robinson (*J. Chem. Soc.*, 1924, **125**, 657—663).—Methylharmaline on oxidation with potassium permanganate in acetone solution yields keto*iso*normethyltetrahydroharmine; acetylharmaline when thus oxidised yields *acetylketotetrahydronorharmine* (III), colourless prisms, m. p. 207—208°, and when reduced with hydrogen in the presence of palladium gives acetyltetrahydroharmaline.









It follows that methyl- and acetyl-harmaline have the constitution (I) and (II). Harmaline methosulphate on treatment with

potassium cyanide gives *cyanomethyltetrahydroharmine*, colourless leaflets, m. p. 155—156°, whilst harmine methosulphate gives a similar but unstable product, m. p. 141°. Acetylketotetrahydronorharmine on hydrolysis with alcoholic potassium hydroxide yields 6-*methoxy*-3-β-*aminoethylindole*-2-*carboxylic acid* (IV), leaflets, decomp. 220—250°, and the corresponding *lactam*, *ketotetrahydronorharmine*, prisms, m. p. 198°. The lactam could not be hydrolysed to the amino-acid, or the latter dehydrated to the lactam. Hydratoacetylharmaline, which forms a *hydrochloride* (+0·5 aq.), colourless needles, on acetylation gives two isomeric *diacetylhydratoacetylharmalines*, (*a*) needles, m. p. 134—135°, (*b*) pale-yellow plates, m. p. 159—160°. The work of O. Fischer (A., 1898, i, 164; 1914, i, 316) is thus confirmed. F. G. M.

Dyes Derived from Phenanthraquinone. IV. Anilinoflavindulines and Phenanthraquinoneazo-dyes. A. C. Sircar and D. C. Roy (*J. Chem. Soc.*, 1924, **125**, 543—547; cf. T., 1913, **103**, 295; 1921, **119**, 1211; 1922, **121**, 1944).—The following phenanthraphenazonium compounds containing an anilino group attached to the benzenoid nucleus did not exhibit the expected property of dyeing in blue shades.

4 : 5-*Dibromo*-11-*anilinoflavinduline chloride*, prepared by reducing nitrosodiphenyl-*m*-phenylenediamine and condensing the product with 4 : 5-dibromophenanthraquinone, green crystals, decomp. 199°, m. p. 245—252°. 2,: 7-*Dinitro*-11-*anilinoflavinduline chloride*, similarly prepared (not crystalline), blackens at 250°, m. p. above 270°. 2-*Nitro*-11-*anilinoflavinduline chloride*, prisms, m. p. above 270°. 2 : 7-*Diamino*-11-*anilinoflavinduline chloride*, bluish-black flocculent precipitate, m. p. above 275°. 4 : 5 : 11-*Trianilinoflavinduline chloride*, prepared from the above 4 : 5-dibromo compound by the action of aniline in the presence of copper powder, is a flocculent precipitate, decomp. 165°, m. p. 205—210°.

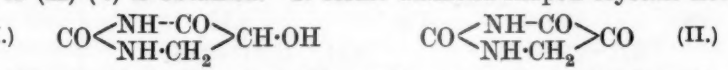
The following azo compounds were prepared by coupling the diazotised aminophenanthraquinone with the hydroxy acid in alkaline solution. 1-Hydroxy-2-naphthoic acid with 2-aminophenanthraquinone gives 4-*hydroxy*-1(2′)-*phenanthraquinoneazo*-3-*naphthoic acid*, m. p. not below 275°; with 4-aminophenanthraquinone gives 4-*hydroxy*-1(4′)-*phenanthraquinoneazo*-3-*naphthoic acid*; with 2 : 7-diaminophenanthraquinone gives *phenanthraquinone*-2 : 7-*bis*(1-*azo*-4-*hydroxy*-3-*naphthoic acid*), m. p. not below 283°; with 4 : 5-diaminophenanthraquinone gives *phenanthraquinone*-4 : 5-*bis*(1-*azo*-4-*hydroxy*-3-*naphthoic acid*), amorphous, m. p. above 275°.

2-Hydroxy-3-naphthoic acid with 2-aminophenanthraquinone gives 2-*hydroxy*-1(2′)-*phenanthraquinoneazo*-3-*naphthoic acid*, blue crystals, decomp. 225°; with 4-aminophenanthraquinone gives 2-*hydroxy*-1(4′)-*phenanthraquinoneazo*-3-*naphthoic acid*, decomp. 250—255°; with 2 : 7-diaminophenanthraquinone gives *phenanthraquinone*-2 : 7-*bis*(1-*azo*-2-*hydroxy*-3-*naphthoic acid*), crystals, m. p. not below 283°; with 4 : 5-diaminophenanthraquinone gives *phenanthraquinone*-4 : 5-*bis*(1-*azo*-2-*hydroxy*-3-*naphthoic acid*), m. p. not

below 274°. Salicylic acid gives with 4-aminophenanthraquinone *phenanthraquinone-4-azosalicylic acid*, m. p. not below 275°; with 2 : 7-diaminophenanthraquinone gives *phenanthraquinone-2 : 7-bisazosalicylic acid*, m. p. not below 270°; with 4 : 5-diaminophenanthraquinone gives *phenanthraquinone-4 : 5-bisazosalicylic acid*, m. p. not below 274°. The dyeing properties on wool of the above compounds and the colours developed in sulphuric acid solution are described. F. G. M.

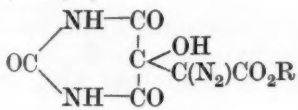
Reaction of Azine and Thiazine Dyes with the Gel of *Chondrus crispus*. E. JUSTIN-MUELLER (*Bull. Soc. chim.*, 1924, **35**, 390—394).—Azine and thiazine dyes coagulate solutions of the gel obtained from lichen carragheen, *Chondrus crispus*. This property is not possessed by the oxazines, and appears to be characteristic of the " az-azonium " and " az-thionium " groupings. R. B.

Catalysis. IV. Behaviour of the Amino Group when Cytosine and Nitrouracil are reduced in the Presence of Colloidal Platinum. E. B. BROWN and T. B. JOHNSON (*J. Amer. Chem. Soc.*, 1924, **46**, 702—708).—Cytosine is reduced by hydrogen in the presence of colloidal platinum with formation of hydrouracil and ammonia. Partial reduction of 5-nitrouracil with three molecular equivalents of hydrogen forms 5-aminouracil, which compound undergoes partial hydrolysis with the production of 5-hydroxyuracil (*iso*barbituric acid); with four molecular equivalents of hydrogen the hydrolysis proceeds further and a new *compound* (I) or (II) (?) is obtained. It forms diamond-shaped crystals not

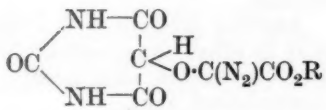


melting at 285°. Yeast-nucleic acid was also submitted to the action of hydrogen in presence of colloidal platinum, and evidence of the formation of ammonia obtained. C. J. S.

Interaction of Ethyl Diazoacetate and Alloxan. H. BILTZ and E. KREMER (*Annalen*, 1924, **436**, 154—173).—Ethyl diazoacetate combines with alloxan to give ethyl dialuryldiazoacetate (I) or (II).



(I.)



(II.)

Formula I best explains the results of methylation (to give trimethyl derivative) and the decomposition effected by alkalis, acids, and oxidising agents. Formula II is also possible, since the ester cannot be acetylated, and since among its reduction products are formed dialuric acid and alloxantin.

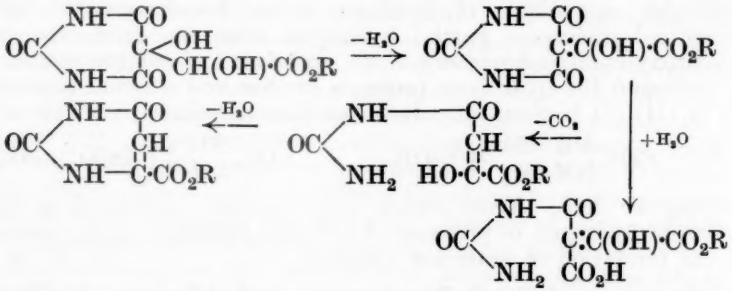
Ethyl dialuryldiazoacetate is produced by the interaction of alloxan hydrate (1 mol.) and ethyl diazoacetate (2·5 mols.), when yellow, six-sided plates, decomp. 163—164°, are obtained. The

disodium salt, $C_8H_6O_6N_4Na_2$, is described. Nitrogen is evolved when the ester is treated with dilute mineral acids or Fehling's solution. *Methyl dialuryldiazoacetate* (from alloxan hydrate and methyl diazoacetate), forms six-sided, yellow needles, decomp. 153—154°.

Ethyl methyl dialuryldiazoacetate (from methylalloxan hydrate) forms prisms, decomp. 136°. Methylalloxan will not give a solid derivative with methyl diazoacetate, whilst dimethylalloxan will not react with either ester.

Methyl 1 : 3 : 5-*trimethyldialuryldiazoacetate* is produced when ethyl dialuryldiazoacetate and diazomethane react in ethereal solution. It forms clusters of prisms, m. p. 99—100°, and when warmed with dilute sulphuric acid affords two atoms of nitrogen. When oxidised with concentrated nitric acid, dimethylalloxan anhydride and oxalic acid are produced; with hydroxylamine, it gives dimethylvioluric acid.

Ethyl dialuryldiazoacetate, on warming with *N*/2-sodium hydroxide, evolves nitrogen, and on acidification, ethyl uracilcarboxylate and carbon dioxide are produced. Uracilcarboxylic acid is also formed in the above reactions, as microscopic needles, m. p. not below 330°, and was characterised as the 5-nitro derivative. The formation of these compounds must take place according to the scheme:



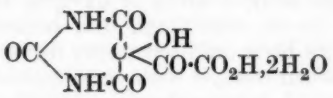
Ethyl dialuryldiazoacetate on hydrolysis with dilute hydrochloric acid yields ethyl glycollate and alloxantin; with concentrated hydrochloric acid, it yields dialuric acid and ethyl glyoxylate.

Another product with either dilute or concentrated hydrochloric acid is ethyl uracilcarboxylate. The methyl ester yields *methyl uracilcarboxylate* (fine needles, m. p. 230°) on hydrolysis with the concentrated acid.

Ethyl 5-*ethoxyuracil*-6-*carboxylate* results from the interaction of dialuryldiazoacetate and alcoholic hydrogen chloride, when nitrogen is evolved, and the ester may be obtained as long, colourless needles, m. p. 203—212°. The *ammonium* salt (pale, rose-coloured plates, m. p. 202—203°) and the *potassium* salt (colourless) are described, and from the latter the free *acid* may be obtained by the action of concentrated hydrochloric acid. It forms colourless prisms, decomposing at 216—217° or on heating at 190°, to give ethyl *iso*barbiturate.

Oxidation of ethyl 5-ethoxyuracil-6-carboxylate with permanganate yields oxaluric and oxalic acids.

Oxidation of ethyl dialuryldiazoacetate with concentrated nitric acid gives alloxan and oxalic acid, and with milder conditions *dialurylglyoxylic acid* dihydrate [microscopic needles, m. p. 152° (decomp.)] may be isolated (annexed formula). With hydrogen peroxide, oxaluric acid is formed.



Reduction of ethyl dialuryldiazoacetate with hydriodic acid gives alloxantin and ethyl iodoacetate, whereas with stannous chloride, the products are dialuric and glycollic acids. A. E. C.

Oxidation of Uric Acid. H. Biltz and H. Schauder (*J. pr. Chem.*, 1923, [ii], **106**, 108—172).—The oxidation of uric acid in dilute acetic acid suspension at 0°, using potassium permanganate (2·6 atoms of oxygen), affords potassium oxalurate and oxalate, carbamide, and oxalyldiureide; when the permanganate used affords 1 atom of oxygen, the same products except the oxalurate are obtained. Oxidation of uric acid with potassium persulphate in presence of potassium acetate is less vigorous than the above and requires water-bath temperatures; when persulphate equivalent to 1 atom of oxygen is used, allantoin results, 2 atoms of oxygen affording potassium oxalurate and oxalyldiureide. Oxidation of uric acid at 0° in aqueous suspension using permanganate (=2 atoms O) in presence of a rapid current of carbon dioxide gives the products obtained by using acetic acid, whilst with permanganate equivalent to 1 atom of oxygen, potassium oxalurate and oxalate and carbamide result. No uroxanic acid is isolated, probably because its precursor, the hypothetical hydroxyacetylenediureinecarboxylic acid, loses carbon dioxide before passing into uroxanic acid.

When uric acid is boiled with aqueous hydrogen peroxide until it is all dissolved, carbonyl dicarbamide is the main product, and is accompanied by a trace of cyanuric acid and a *substance* forming white, hemispherical masses, decomp. 220°. The results are unaffected by adding small quantities of acetic acid or of potassium acetate.

Oxidation of uric acid by permanganate (=1 atom O) at the ordinary temperature in presence of sulphuric acid gives alloxan and alloxantin, whilst if the acid is boiled with aqueous potassium persulphate solution (=1 atom O) alloxan is formed in small quantities, the majority of the acid probably passing into alloxanic acid and the latter into 5-hydroxyhydantoin (A., 1921, i, 815). When twice the above proportion of persulphate is used, a little parabanic acid is formed, presumably from alloxan.

Hydrogen peroxide converts uric acid in presence of boiling dilute sulphuric acid into parabanic acid (formed from alloxan). In presence of boiling dilute hydrochloric acid, the oxidation is so satisfactory that the author recommends this as a method of preparing parabanic acid.

Possible intermediate compounds in the oxidation of uric to oxaluric acid are uric acid glycol, alloxan, allantoin, or the hypothetical hydroxyacetylenediureinecarboxylic acid. These compounds require for their formation (from uric acid) 1 atom of oxygen, this amount of oxygen being required to convert them into oxaluric acid. The compounds have therefore been oxidised under different conditions. Uric acid 4 : 5-glycol, when treated with permanganate (=1 atom O) in dilute acetic acid at 0°, is very slowly oxidised and affords impure potassium oxalurate and oxalate. In boiling solution, oxidation is rapid, but the yield of oxalurate is small. The glycol is therefore not the intermediate between uric and oxaluric acids.

9-Methyluric acid 4 : 5-glycol, oxidised with permanganate and acetic acid in the warm, gives methyloxaluric acid (?), m. p. 180—190° (with frothing). 7 : 9-Dimethyluric acid 4 : 5-glycol similarly affords small quantities of dimethylparabanic acid.

Alloxan is very slowly oxidised by cold permanganate and dilute acetic acid to give potassium oxalurate. Oxidation is more rapid in the warm, but alloxan is clearly not the intermediate sought for. Hydrogen peroxide oxidises alloxan at water-bath temperatures to give oxaluric acid.

Allantoin is slowly oxidised by cold and rapidly by warm permanganate, potassium oxalurate and carbamide resulting. Allantoin is ruled out as the intermediate oxidation product, which is evidently the hypothetical hydroxyacetylenediureinecarboxylic acid.

A method is given for the preparation of potassium oxalurate from uric acid and consists in the oxidation of the latter in alkaline solution, and then in acetic acid solution, using permanganate equivalent to one atom of oxygen for each stage. Potassium oxalurate ($C_3H_3O_4N_2K,H_2O$), when treated with hydrochloric acid, affords *oxaluric acid*, decomp. 208—210°. The *ammonium* salt is described. *Methyl oxalurate*, from the acid and diazomethane, forms crystals, m. p. 192° (indef. with frothing). *Oxaluric methylamide*, from the ester and aqueous methylamine, forms needles, decomp. 251—253°. When oxaluric acid is boiled for a short time with water, carbamide oxalate and ammonium tetraoxalate result. The monocarbamide oxalate described by Lubavin (1872) does not exist. If equimolecular quantities of carbamide and oxalic acid are mixed in aqueous solution, carbamide oxalate, $H_2C_2O_4,2CO(NH_2)_2$, separates, whilst if the solution is boiled for some time, ammonium oxalate is formed.

When 1 : 3-dimethyluric acid is oxidised with alkaline permanganate (=1 atom O), potassium oxalurate and *s*-dimethyloxamide result. Alkaline oxidation (1 atom O) followed by acid oxidation (acetic; 1 atom O) affords potassium oxalurate and dimethylparabanate, together with *s*-dimethyloxamide and oxaluric methylamide. Oxidation (1 atom O) in acetic acid solution gives dimethylparabanic acid and a crystalline *substance* (not examined), oxidation with 2 atoms of oxygen (as permanganate) affording potassium oxalurate and dimethylparabanic acid. Oxidation of 1 : 3-dimethyl-

uric acid with alkaline hydrogen peroxide affords a *substance* forming needles, m. p. 215° (decomp.).

3 : 7-Dimethyluric acid when oxidised by alkaline permanganate (1 atom O) gives 1 : 8-dimethylallantoin together with a *potassium* salt, $C_6H_4O_5N_3K$, plates, m. p. 275° (indef. and decomp.) (corresponding with an *acid*, $C_6H_5O_5N_3$, prisms, decomp. 212°). 3 : 7-Dimethyluric acid is converted by alkaline hydrogen peroxide into carbonyl dicarbamide (?), decomp. 210°.

No alloxan is formed when chlorine is passed into a suspension of uric acid in aqueous sodium acetate–acetic acid. No alloxans are formed when 9-methyluric acid glycol is heated with hydrochloric acid, the products being carbamide and methylparabanic acid. Similarly treated, 7 : 9-dimethyluric acid glycol affords carbamide and dimethylparabanic acid. The glycol type is therefore not intermediately formed when uric acids are oxidised to alloxans.

5-Chloro- and 5-hydroxy-ψ-uric acids are readily converted by hydrochloric acid into alloxan, which is conveniently identified by adding stannous chloride and isolating alloxantin.

The chloraluric acid described by Schiel (1859) is, as stated by Lubavin (*loc. cit.*), a mixture of ammonium chloride and parabanic acid. The stryphnic acid obtained by Gibbs (1869) on treating uric acid with potassium nitrite and mineral acid, is now shown to be a mixture of allantoin with oxaluric and oxalic acids. Similarly, the urinilic acid described by Sokolov (1869) does not exist; nitric oxide has no action on an aqueous suspension of uric acid, whilst nitrogen peroxide has no action on uric acid in absence of water; nitric oxide containing a little nitrogen peroxide converts uric acid, in aqueous suspension, into uric acid glycol, parabanic acid, and alloxan, whilst nitric oxide containing much nitrogen peroxide affords xanthine, parabanic acid, alloxan, and oxalic acid.

The paper contains a useful discussion of the results obtained.

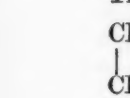
E. E. T.

Potassium Hydroxyhæmin. A. Hamsik (*Z. physiol. Chem.*, 1924, **133**, 173—179).—The author has previously (*Spisy lékařské fakulty v Brně*, 1922, **1**, 1A, 5), by extracting the coagulum of blood with alcohol acidified with oxalic acid, obtained a compound $C_{34}H_{31}O_4N_4Fe$, small star-like aggregates of crystals, which he named hydroxyhæmin anhydride. By boiling the anhydride with glacial acetic acid and sodium chloride or with alcohol, oxalic acid, and sodium chloride, α-chlorohæmin was obtained. Potassium hydroxyhæmin, $C_{34}H_{30}O_4N_4K_2Fe{\cdot}OH$, very small spherical, crystalline aggregates, was obtained by treating hydroxyhæmin anhydride or α-chlorohæmin with alcoholic potassium hydroxide.

S. S. Z.

A New Type of Cyclic Compound. E. P. Kohler (*J. Amer. Chem. Soc.*, 1924, **46**, 503—517; cf. A., 1916, i, 404; 1919, i, 582).—Improved methods are described for the preparation of phenyl γ-nitro-β-phenylpropyl ketone and of its α-bromo derivative, which occurs in two stereoisomeric forms, needles, m. p. 108°, and plates

or prisms, m. p. 129°, and is accompanied, in its formation, by the *αα-dibromo* derivative, tablets, m. p. 106°. The α-bromo derivative, when treated with potassium acetate in methyl-alcoholic solution, affords a mixture of the *cyclo*propane derivative previously described with *2-hydroxy-3-methoxy-5-benzoyl-4-phenylisoxazolidine* and an unidentified oxazole (?) derivative. If the isoxazolidine (prisms, m. p. 162°) is dissolved in glacial acetic acid and the solution poured into water, *2 : 3-dihydroxy-5-benzoyl-4-phenylisoxazolidine*, prisms, m. p. 153°, results (*dibenzoyl* derivative, tablets, m. p. 158—160°). The isoxazolidine (m. p. 162°), when treated with ammonia, affords *3-amino-2-hydroxy-5-benzoyl-4-phenylisoxazolidine*, needles, m. p. about 162° (decomp.); this substance, when boiled with ethyl alcohol in presence of acetic acid, being converted into *2-hydroxy-3-ethoxy-5-benzoyl-4-phenylisoxazolidine*, m. p. 168° (decomp.), boiling with methyl alcohol etc. affording the above methoxy compound. The latter, when treated with acetic anhydride, is slowly converted into *phenyl γ-nitro-α-acetoxy-β-phenylpropyl ketone* (tablets, m. p. 98°), which with ammonia affords the corresponding *α-hydroxy* compound (m. p. 142°; *benzoyl* derivative, needles, m. p. 106—107°). The last-named hydroxy compound, when treated with hydrogen chloride in methyl-alcoholic solution, is converted into the methoxyisoxazolidine of m. p. 162°. The formation from the latter of the above ketone (m. p. 98°) takes place through the intermediate production of *5-benzoyl-4-phenylisoxazoline oxide*, colourless tablets, m. p. 126° (annexed formula). This compound, which results when the above α-bromoketone is treated with potassium acetate in *iso*propyl-alcoholic solution, combines with water, and with primary (but not with secondary) alcohols, in presence of acid, to give isoxazolidines, water, *e.g.*, affording the dihydroxyisoxazolidine mentioned above, whilst ammonia affords the above aminohydroxyisoxazolidine. The isoxazolidines described form sparingly soluble copper salts. The methoxyisoxazolidine, which is converted at its m. p. into methyl alcohol, water, benzonitrile, and a nitrogenous substance, affords a *benzoyl* derivative (colourless plates, m. p. 114°) and a *copper* derivative, $C_{17}H_{17}O_5NCu$, and (like the isoxazoline oxide) is converted by alkali into benzonitrile, and formic and phenylacetic acids.



A. B. S.

Indoxazens and *iso*Oxazoles. K. VON AUWERS (*Ber.*, 1924, **57**, [*B*], 461—467).—A comparison of the optical properties of indoxazen with those of *iso*oxazole and its derivatives confirms the structure, $C_6H_4<\begin{matrix}CH\\O\end{matrix}>N$, ascribed to the former compound by Conduché (A., 1908, i, 154). The following data, amongst others, are recorded. *iso*Oxazole, b. p. 95°, d_4^{20} 1·078, n_{He}^{20} 1·428. 5-Methyl-*iso*oxazole, b. p. 122°, d_4^{20} 1·023, n_{He}^{20} 1·439. 3-Methyl*iso*oxazole, b. p. 118°, d_4^{20} 1·022, n_{He}^{20} 1·435. 3 : 5-Dimethyl*iso*oxazole, b. p. 143°, d_4^{20} 0·983, n_{He}^{20} 1·442. 3 : 4 : 5-Trimethyl*iso*oxazole, b. p. 111°/75 mm., d_4^{20} 0·981, n_{He}^{20} 1·452. 3 : 4-Tetramethylene*iso*oxazole,

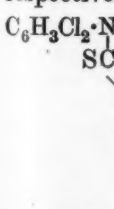
$C_6H_8\langle\begin{smallmatrix}CH\\N\end{smallmatrix}\rangle O$, b. p. 93°/15 mm., d_4^{20} 1·095, n_{He}^{20} 1·498. Methyltetrahydrobenzo-3 : 4-*iso*oxazole, b. p. 97°/16 mm., d_4^{20} 1·059, n_{He}^{20} 1·491. Methyltetrahydrobenzo-4 : 5-*iso*oxazole, b. p. 101°/18 mm., d_4^{20} 1·062, n_{He}^{20} 1·492.

Indoxazen, b. p. 84°/11 mm., d_4^{20} 1·170, n_{He}^{20} 1·563. 3-Phenylindoxazen, $C_6H_4\langle\begin{smallmatrix}CPh\\O\end{smallmatrix}\rangle N$, m. p. 83—84°, b. p. 181°/13 mm., $d_4^{39·9}$ 1·1241, $n_{He}^{39·9}$ 1·59279. Salicylonitrile, $d_4^{39·6}$ 1·1052, $n_{He}^{39·6}$ 1·54359. *o*-Methoxybenzonitrile, b. p. 146°/20 mm., d_4^{20} 1·107, n_{He}^{20} 1·548. *o*-Anisaldoxime methyl ether, b. p. 235°, d_4^{20} 1·092, n_{He}^{20} 1·554.

Attempts to convert *o*-aminoacetophenone into 3-methylindoxazen gave unexpectedly methylanthranil, $C_6H_4\langle\begin{smallmatrix}CMe\\N\end{smallmatrix}\rangle O$, b. p. 121°/17 mm., $d_4^{23·2}$ 1·1304, $n_{He}^{23·2}$ 1·57457. H. W.

Synthesis of Thiobiazolone Derivatives. C. Bülow and F. Seidel (*Ber.*, 1924, **57**, [*B*], 357—362).—Thiobiazolone sulphides may be obtained simply by the action of potassium xanthate on the 2 : 4-dichlorophenylhydrazone of ethyl α-chloroglyoxylate and analogous substances (cf. Bülow and Neber, A., 1913, i, 207, 999; 1916, i, 845).

The 2 : 4-dichlorophenylhydrazone of ethyl α-chloroglyoxylate, $C_6H_3Cl_2\cdot NH\cdot N{:}CCl\cdot CO_2Et$, is converted by potassium xanthate in warm alcoholic solution into *ethyl 5-thio-4-op-dichlorophenyl-thiobiazolone-2-carboxylate*, $\begin{smallmatrix}N(C_6H_3Cl_2)\cdot CS\\ N{=}C(CO_2Et)\end{smallmatrix}\rangle S$, small, colourless needles, m. p. 122°, which is transformed by an alcoholic solution of ammonia into the corresponding *amide*, $C_9H_5ON_3S_2Cl_2$, colourless needles, m. p. 235°; the hydrolysis of the ester or amide to the acid could not be effected. A *substance*, $C_{21}H_{16}O_4N_4Cl_4S_2$, m. p. 158—160° or 173° (when crystallised from alcohol or acetic acid, respectively) is obtained as by-product of the preparation of the ester. The latter compound is converted by prolonged treatment with an excess of hydrazine hydrate in boiling alcoholic solution into the *triazole* derivative,



$\begin{smallmatrix}N{=}{=}{=}{=}{=}CH\\ N(C_6H_3Cl_2)\cdot CS\end{smallmatrix}\rangle N\cdot NH_2$,

colourless needles, m. p. 153°; under somewhat different conditions, a *product*, $C_9H_6ON_6Cl_2S$, colourless needles, m. p. 196—197° (decomp.) after softening at 191—192°, is obtained, to which the annexed constitution is ascribed.

When acetone is used as solvent in place of alcohol, the action between potassium xanthate and the 2 : 4-dichlorophenylhydrazone of ethyl α-chloroglyoxylate follows a different course and leads to the production of the *sulphide*, $S[C(CO_2Et){:}N\cdot NH\cdot C_6H_3Cl_2]_2$, hygroscopic crystals, m. p. 175—176°, which can also be obtained by the action of ammonium sulphide on the chloro ester.

2 : 4-Dichlorophenylhydrazonopyruvyl chloride does not appear

to be convertible by potassium xanthate into a thiobiazolone; it is transformed by potassium xanthate or colourless ammonium sulphide in the presence of acetone into the *sulphide*,

$$S(CAc{:}N{\cdot}NH{\cdot}C_6H_3Cl_2)_2,$$

a yellow substance, m. p. 220—222° (decomp.) after becoming black at about 180°. H. W.

o-Hydroxyazoxy Compounds. D. Bigiavi and R. Poggi (*Gazzetta*, 1924, **54**, 114—131).—The authors have investigated the pairs of isomeric azoxy compounds obtained from benzeneazo-*p*-cresol and its derivatives when these are oxidised by means of peracetic acid. That *p*-hydroxyazo compounds exhibit the hydroxylic and not the quinonephenylhydrazonic structure was shown by McPherson (A., 1896, i, 27; 1900, i, 123) and by Willstätter and Veraguth (A., 1907, i, 453), who found that the acyl derivatives of benzeneazophenol are different from the compounds resulting from benzoquinone and the *as*-acylphenylhydrazines. For the corresponding ortho compounds no such difference has been encountered, and their tardy solubility in alkali, their failure to react with ammonia in an anhydrous solvent, and various other physico-chemical considerations incline certain authors (cf. Farmer and Hantzsch, A., 1900, i, 122; Puxeddu and Gennari, A., 1922, i, 587) to prefer the quinonoid to the hydroxyazoic structure for *o*-hydroxyazo derivatives.

The assumption of different constitutions for *o*- and *p*-hydroxyazo compounds seems, however, unwarranted, and, indeed, in many reactions benzeneazo-*p*-cresol behaves similarly to *p*-hydroxyazobenzene. Thus, its ready formation of two isomeric azoxy compounds is not easy to explain on the basis of the quinonoid structure. Moreover, the similarity is borne out by (1) the formation of unstable hydrazophenols when the *o*-hydroxyazo compounds are reduced by either aluminium amalgam in ethereal solution or zinc and ammonium chloride, (2) the formation, by the action of nitrous acid, of a nitro derivative containing the nitro group in the cresol nucleus, and the formation of bisbenzeneazo-*p*-cresol (cf. Puxeddu and Maccioni, A., 1907, i, 798) by the action of a normal diazotate.

The structures of the two benzeneazoxycresols are determined as follows. When treated with bromine, the one, m. p. 125°, yields a dibromo derivative with a bromine atom in each nucleus, since it gives *p*-bromoaniline and 3-bromo-6-amino-*p*-cresol on reduction; the other, m. p. 74°, gives a monobromo derivative and then a polybromo derivative which has bromine in only the cresol nucleus, as the only base volatile in a current of steam formed on reduction is aniline. It may be assumed, therefore, that the former isomeride contains the residue NPh: and is the β-compound, and the latter, O:NPh:, and is the α-compound. The following observations, confirmatory of these conclusions, have been made.

Nitrous acid does not react with β-benzeneazoxycresol, but with the α-isomeride readily forms a nitro derivative which has the

nitro group in the cresol nucleus and in the ortho-position towards the hydroxyl group, as it reacts with diazonium salts to form an azoazoxy derivative. Benzene-α-azoxycresol is readily oxidised by permanganate to *iso*diazobenzene and, probably, to *o*-nitrocresol; with the β-isomeride, the oxidation is extremely slow, although Bamberger gave this reaction as a means of recognising azoxyphenols. The pale yellow α-compound changes moderately rapidly to chestnut-yellow under the influence of light, but the β-isomeride retains its colour almost unaltered. Etherification of the hydroxyl proceeds normally with the α-, but with great difficulty with the β-form. The structure attributed by Baudisch (A., 1917, i, 356) to the β-*o*-hydroxyazoxybenzenes is regarded as unauthorised.

The *nitro* derivative of benzeneazocresol ($N_2 : OH : NO_2 : Me = 1 : 2 : 3 : 5$) crystallises in dark red, lustrous, plush-like needles, m. p. 130°, and is oxidised with difficulty by peracetic acid, yielding a mixture, m. p. 110°, of the two nitroazoxy compounds.

Benzene-α-azoxycresol, O:NPh:N·C_6H_3Me·OH, forms transparent, orange prisms, m. p. 73—74°, and gives a deep, blood-red coloration with concentrated sulphuric acid. Its *acetyl* derivative separates in yellow needles or transparent, prismatic crystals, m. p. 78—79°, and yields acetylhydrazocresol when reduced by means of aluminium amalgam in ethereal solution. Its *benzoyl* derivative forms pale yellow prisms, m. p. 97—101°.

Benzene-α-azoxy-m-*nitro*-p-*cresol*, O:NPh:N·C_6H_2(Me)(OH)NO_2, crystallises in yellow, silky needles, m. p. 121—122°, and dissolves in alkali hydroxide or carbonate solution to a blood-red solution.

Benzeneazobenzene-α-azoxy-p-*cresol*,

O:NPh:N·C_6H_2(Me)(OH)·N_2Ph,

forms long, silky needles, m. p. 148—149°, which are almost black when moistened with benzene, but brilliant chestnut-yellow when dry. With concentrated sulphuric acid, it gives a reddish-brown coloration, and with sodium hydroxide solution containing a few drops of alcohol an intense violet coloration turning to reddish-violet when the liquid is diluted.

Benzene-α-azoxy-m-*bromo*-p-*cresol* crystallises in lustrous, sulphur-yellow needles, m. p. 143—144°, and dissolves in sodium hydroxide solution to a bright red solution. When brominated further, it yields the *polybromo* derivative, $C_{13}H_7O_2N_2Br_5$, which crystallises in silky, yellow needles, m. p. 164—165°.

Benzene-β-azoxycresol, NPh:NO·C_6H_3Me·OH, crystallises in lustrous, yellow needles, m. p. 70—72°; its yellow *benzoyl* derivative has m. p. about 56°, and its *acetyl* derivative was obtained only as a dense, non-crystallising oil.

Benzene-β-azoxynitrocresol, NPh:NO·C_6H_2Me(OH)·NO_2, forms yellow, acicular prisms, m. p. 117—119°, and yields aniline when reduced with tin and hydrochloric acid.

Benzene-β-azoxybromocresol, NPh:NO·C_6H_2MeBr·OH, forms chestnut-yellow, silky needles, m. p. 117°.

p-*Bromobenzene-β-azoxybromocresol*, C_6H_4Br·N:NO·C_6H_2MeBr·OH, crystallises in golden-yellow, silky needles, m. p. 166—167°, is turned scarlet and dissolved by alkali hydroxide solution, and

yields bromoaniline and bromoaminocresol (cf. Thiele and Eichwede, A., 1900, i, 501) on reduction. T. H. P.

NN′-Dimethylenesulphurous Acid-3 : 3′-diamino-4 : 4′-dihydroxyazobenzene. W. G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1924, **46**, 497—503).—*NN′-Dimethylenesulphurous acid-3 : 3′-diamino-4 : 4′-dihydroxyazobenzene*, $C_{14}H_{16}O_8N_4S_2$, was isolated by the addition of formaldehyde and sodium bisulphite to the solution of the dihydrochloride of the 3 : 3′-diamino-4 : 4′-dihydroxyazobenzene prepared by the reduction of the corresponding nitro compound in an atmosphere of carbon dioxide. The *sodium*, *magnesium*, and *barium* salts are described. Contrary to expectations, the substance was physiologically inactive. A. B. S.

Absorption Spectra of certain Derivatives of *p*-Cymene. W. C. HOLMES (*J. Amer. Chem. Soc.*, 1924, **46**, 631—635).—The general effect of introducing methyl and *iso*propyl groups into a number of azo dyes of the benzene series is to shift the absorption band towards a region of longer wave-length, the displacement of the maximum being about 10 $\mu\mu$.

Introduction of the *iso*propyl group into Victoria green (malachite green) in the non-aminated nucleus in the *p*-position to the methane carbon atom produces a converging displacement of the two absorption bands in the visible spectrum. Both bands gradually disappear in sulphuric acid solution, and give rise to a new band, that of the *di*-acid salt, in the same spectral region as the second band of the neutral solution. The absorption bands of phenolsulphonephthalein and the homologue containing the *iso*propyl group in the sulphonated residue are practically identical, and absorption measurements in buffered solutions show that as p_H is lowered the transition between the absorption forms characteristic of alkaline and neutral solutions occurs more rapidly with the higher homologue than with the parent substance. S. K. T.

Azo Dyes from *m*-Methylethylbenzene. A. MAILHE (*Bull. Soc. chim.*, 1924, **35**, 382—383).—The following dyes have been prepared from 6-amino-1-methyl-3-ethylbenzene (cf. A., 1921, i, 661): *2-methyl-4-ethyl-4′-hydroxyazobenzene*, a brown powder; *1-methyl-3-ethylbenzene-6-azo-β-naphthol*, a red powder; *1-methyl-3-ethylbenzene-6-azo-β-naphthylamine*, a maroon powder; *1-methyl-3-ethylbenzene-6-azo-α-naphthylamine*, a greenish mass; *1-methyl-3-ethylbenzene-6-azodimethylaniline*, a brown powder; from Schäffer salt, *1-methyl-3-ethylbenzene-6-azo-β-naphthol-6-sulphonic acid*, dark brown, dyeing maroon on silk; from R-salt, *1-methyl-3-ethylbenzene-6-azo-β-naphthol-3 : 6-disulphonic acid*, a red powder, dyeing silk a fast ponceau; from crocein acid, *1-methyl-3-ethylbenzene-6-azo-β-naphthol-8-sulphonic acid*, a maroon powder, giving maroon shades on silk. From G-salt, *1-methyl-3-ethylbenzene-6-azo-β-naphthol-6 : 8-disulphonic acid*, dark yellow powder, dyeing maroon shades on silk; and from H-acid, *1-methyl-3-ethylbenzene-6-azo-8-amino-α-naphthol-3 : 5-disulphonic acid*, reddish-scarlet, giving fast reddish-ponceau shades on silk. R. B.

Colour and Constitution. I. Effect of Isomerism on the Colour of certain Azo Dyes. M. L. CROSSLEY and P. V. RESENVELT (*Ind. Eng. Chem.*, 1924, **16**, 271—273).—Sodium benzeneazo-β-naphthol-6-sulphonate is a reddish-orange dye. If the sulphonic group passes to positions 7 and 8, the colour becomes progressively more yellow. The 3 : 6-disulphonic acid salt is more red, the 6 : 8-disulphonic acid salt more yellow than any of the monosulphonates. Further systematic colour modifications are caused by substitution within the benzene ring. There is also a great difference between the reactivities of the two β-naphtholdisulphonic acids, the presence of the sulphonic group in position 8 appearing to reduce the reactivity of the hydrogen in position 1, by neutralising the effect of the adjacent hydroxyl group. These facts are discussed in terms of the "force-field" and additive theories of chemical reactions. The relation between the effect on colour and the effect on reactivity of the position of the sulphonic group is held to be significant. [Cf. *B.*, 1924, 368.] C. I.

***m*-Nitrocinnamic Acid Hydrazide and its Behaviour with Nitrous Acid.** T. CURTIUS and P. A. BLEICHER (*J. pr. Chem.*, 1924, [ii], **107**, 86—98; cf. A., 1909, i, 838; 1911, i, 682, 814).—The action of hydrazine hydrate on ethyl *m*-nitrocinnamate gives, in addition to the main product of the reaction, m-*nitrocinnamic acid hydrazide*, $NO_2 \cdot C_6H_4 \cdot CH{:}CH \cdot CO \cdot NH \cdot NH_2$ (bright yellow, anisotropic plates, m. p. 139°), an isomeric substance, bright yellow needles, m. p. 198°, which with nitrous acid yields a true azide (see following abstract). *m*-Nitrocinnamic acid hydrazide when treated with iodine and sodium hydrogen carbonate in alcoholic solution is converted into a *dihydrazide*,

$$(NO_2 \cdot C_6H_4 \cdot CH{:}CH \cdot CO \cdot NH \cdot)_2,$$

pale yellow, prismatic needles, m. p. 279° (decomp.). The *hydrochloride*, tablets, m. p. 212° (decomp.), with benzaldehyde gives *benzylidene*-m-*nitrocinnamic acid hydrazide*, minute needles, m. p. 206·5°, whilst benzoyl chloride yields *benzoyl*-m-*nitrocinnamic acid hydrazide*, $NO_2 \cdot C_6H_4 \cdot CH{:}CH \cdot CO \cdot NH \cdot NHBz$, prisms, m. p. 185·5°. With ethyl acetoacetate, *m*-nitrocinnamic acid hydrazide yields the *compound*, $NO_2 \cdot C_6H_4 \cdot CH{:}CH \cdot CO \cdot NH \cdot N{:}CMe \cdot CO_2Et$, white, fibrous needles, m. p. 67·5°, and with phenylthiocarbimide m-*nitrocinnamylphenylthiosemicarbazide*,

$$NO_2 \cdot C_6H_4 \cdot CH{:}CH \cdot CO \cdot NH \cdot NH \cdot CS \cdot NHPh,$$

pale yellow plates, m. p. 147°. Sodium nitrite readily converts the hydrochloride into 1-*nitroso*-5-m-*nitrophenyl*-3-*pyrazolidine*, yellow, prismatic plates, m. p. 108° (*ammonium*, *silver*, and *barium* salts described). The silver salt on treatment with ethereal ethyl iodide gives 1-*nitroso*-2-*ethyl*-5-*m*-*nitrophenyl*-3-*pyrazolidine*, greyish plates, m. p. 168°. The ammonium salt of 1-nitroso-5-*m*-nitrophenyl-3-pyrazolidine gives a *picrate*, m. p. 107—108°. The action of bromine on 1-nitroso-5-*m*-nitrophenyl-3-pyrazolidine in acetic acid solution gives 4-*bromo*-3-m-*nitrophenyl*-5-*pyrazoline*, yellow plates, m. p. 188°, only one bromine atom entering the ring, whereas the action of bromine on 1-nitroso-5-phenyl-3-pyrazolidine

gives 4 : 4-dibromo-3-phenyl-5-pyrazolone. On boiling with dilute sulphuric acid, the 1-nitroso-5-*m*-nitrophenyl-3-pyrazolidine is converted into 3-m-*nitrophenyl*-4-*isonitroso*-5-*pyrazoline*, orange, silky needles, m. p. 217°.

The isomeric *m*-nitrocinnamic acid hydrazide, of m. p. 198°, gives a *benzylidene* derivative, m. p. 184°, and a *hydrochloride*, m. p. 256° (decomp.). R. B.

***m*-Nitrocinnamic Acid Azide.** T. CURTIUS and E. KENNGOTT (*J. pr. Chem.*, 1924, [ii], **107**, 99—102).—The isomeric *m*-nitrocinnamic acid hydrazide of m. p. 198° formed as a by-product in the action of hydrazine hydrate on *m*-nitrocinnamic ester (see preceding abstract) on treatment with nitrous acid gives m-*nitrocinnamic acid azide*, $NO_2 \cdot C_6H_4 \cdot CH:CH \cdot CO \cdot N_3$, colourless, rhombic crystals (m. p. 117—118°, with evolution of gas), which are converted into *m*-nitrocinnamic acid when warmed with alkali. When warmed with *p*-toluidine in alcoholic solution, the azide gives *p*-tolyl *m*-nitrostyrylcarbamide,

$$NO_2 \cdot C_6H_4 \cdot CH:CH \cdot HN \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_3,$$

bright yellow needles, m. p. 213—214°. Boiling with water converts the azide into nitrogen, carbon dioxide, and a colourless carbamide (?), m. p. 186°. Boiling with methyl alcohol gives the known methyl *m*-nitrostyrylcarbamate,

$$NO_2 \cdot C_6H_4 \cdot CH:CH \cdot NH \cdot CO \cdot OMe,$$

yellow needles, m. p. 140°, which when boiled with dilute sulphuric acid give *m*-nitrophenylacetaldehyde. The interconversion of *m*-nitrocinnamic acid hydrazide, m. p. 139°, and the isomeric compound, m. p. 198°, can be effected either by heating above the melting point or by warming in alcoholic solution or under pressure. R. B.

Salts with *para*-, *ortho*-, and *meta*-Quinonoid Structure. V. R. CIUSA and G. RASTELLI (*Gazzetta*, 1924, **54**, 72—78; cf. A., 1922, i, 1073).—*p*-Nitrophenylmethylhydrazones,

$$CHR:N \cdot NMe \cdot C_6H_4 \cdot NO_2,$$

of the following aldehydes have been prepared: *Formaldehyde*, dark yellow crystals, m. p. 153°, separating even from solutions containing the aldehyde in the proportion 1 : 10,000; *acetaldehyde*, yellow needles, m. p. 91°; *butyraldehyde*, yellow crystals, m. p. 05° (?); p-*tolualdehyde*, yellow, tabular crystals, m. p. 150°; o-*nitrobenzaldehyde*, orange-yellow, acicular crystals, m. p. 211—212°; m-*nitrobenzaldehyde*, lemon-yellow crystals, m. p. 250°; p-*nitrobenzaldehyde*, orange-yellow crystals, m. p. 249—250°; *cuminaldehyde*, yellow crystals with violet reflection, m. p. 112°; *dimethylaminobenzaldehyde*, bright red needles, m. p. 193°; *cinnamaldehyde*, dark yellow needles, m. p. 153—154°; *salicylaldehyde*, dark yellow needles, m. p. 150°; p-*hydroxybenzaldehyde*, red crystals, m. p. 204°; *anisaldehyde*, small, yellow crystals, m. p. 155—156°; *protocatechualdehyde*, bright red crystals, m. p. 218°; *vanillin*, m. p. 182°, existing in yellow and red chromoisomeric modifications; *piperonaldehyde*, yellow crystals, m. p. 190—191°; 2 : 4-*dihydroxybenzaldehyde*, deep red crystals, m. p. 265°; 2-*hydroxy*-4-*methoxy*-

benzaldehyde, lustrous, yellow needles, m. p. 148°, existing also in a red modification; *furfuraldehyde*, orange-yellow, crystalline plates, m. p. 171°; *pyrrolealdehyde*, bright red, acicular crystals, m. p. 177°; *acetone*, silky, yellow needles, m. p. 54°; cyclo*hexanone*, yellow crystals, m. p. 186°. The *mono*-p-*nitrophenylmethylhydrazone* of *diacetyl* forms brownish-yellow needles, m. p. 154°, that of *acetylacetone*, lustrous, orange needles, m. p. 128°, and that of *acetonylacetone*, yellow needles, m. p. 130°.

Benzaldehyde-p-*nitrophenylethylhydrazone*,

$$CHPh{:}N{\cdot}NEt{\cdot}C_6H_4{\cdot}NO_2,$$

obtained by the action of ethyl iodide on the potassium salt of benzaldehyde-*p*-nitrophenylhydrazone, forms large, yellow crystals, m. p. 134°. When boiled with hydrochloric acid it yields as-p-*nitrophenylethylhydrazine*, $NH_2{\cdot}NEt{\cdot}C_6H_4{\cdot}NO_2$, which crystallises in lustrous, yellow leaflets, m. p. 74°, and energetically reduces Fehling's and ammoniacal silver solutions. p-*Nitrobenzaldehyde*-p-*nitrophenylethylhydrazone* crystallises in yellow needles, m. p. 267°.

Benzaldehyde-p-*nitrophenylbenzylhydrazone*, $C_{20}H_{17}O_2N_3$, prepared from benzyl chloride and the potassium derivative of benzaldehyde-*p*-nitrophenylhydrazone, forms lustrous, yellow, laminar crystals, m. p. 158°, and as-p-*nitrophenylbenzylhydrazine*, $C_{13}H_{13}O_2N_3$, which reduces Fehling's solution and ammoniacal silver solution, yellow needles, m. p. 121°. T. H. P.

[**Aromatic Arsenious Acids.**] A. Albert (U.S. Pat. 1472778).—Nitroaminohydroxyacetophenone, when diazotised and treated in alkaline solution with sodium arsenite, yields nitrohydroxyacetylphenylarsinic acid, $CH_3{\cdot}CO{\cdot}C_6H_2(OH)(NO_2){\cdot}AsO_3H_2$, needles, m. p. about 200°. Similarly, *p*-aminobenzophenone yields benzoylphenylarsinic acid, m. p. 195—197°, diaminobenzophenone yields the diarsinic acid compound, m. p. 260°, and *p*-aminobenzaldehyde yields *p*-aldehydophenylarsinic acid.

Chemical Abstracts.

Tin Di*cyclo*hexyl, Hexa*cyclo*hexyldistannane, and other *cyclo*Hexyl Compounds of Tin. E. Krause and R. Pohland (*Ber.*, 1924, **57**, [*B*], 532—544).—An extension of the work on the organo-metallic derivatives of tin (Krause and Becker, A., 1920, i, 340) to the *cyclo*hexyl series. The *cyclo*hexyl bromide used had b. p. 52·5°/13·5 mm., $d_4^{16\cdot8}$ (vac.) 1·3348, $n_D^{16\cdot8}$ 1·49758, whereas *cyclo*hexyl chloride had b. p. 141°/760 mm., $d_4^{20\cdot3}$ 1·0000, $n_D^{20\cdot3}$ 1·46264.

Tin tetra*cyclo*hexyl, $Sn(C_6H_{11})_4$ (cf. Grüttner, A., 1915, i, 335) is prepared by the gradual addition of a solution of stannic chloride in benzene to a solution of magnesium *cyclo*hexyl bromide or chloride in a mixture of ether and benzene. The product is a mixture of tin tetra*cyclo*hexyl, hexa*cyclo*hexyldistannane, and halogenated substances which cannot be separated into its components by crystallisation except with great loss of material; it is therefore converted into the monobromide (see later), which is readily purified and subsequently transformed by magnesium *cyclo*hexyl bromide into the tetra derivative, which crystallises in

colourless, quadratic platelets, m. p. 263—264° after slight previous softening (Grüttner gives m. p. 248°).

Tin dicyclohexyl, $Sn(C_6H_{11})_2$, prepared from stannous chloride and magnesium *cyclo*hexyl bromide, is an intensely yellow, voluminous powder, melting to a red liquid at 176—178° after darkening at 130°. It is stable in an atmosphere of nitrogen, but gradually oxidises in air, particularly under the influence of light. It is converted by *cyclo*hexyl bromide at 140° into tin di*cyclo*hexyl dibromide. Attempts to convert it into hexa*cyclo*hexyldistannane by means of magnesium *cyclo*hexyl bromide (cf. A., 1920, i, 341) were unsuccessful.

Hexacyclohexyldistannane, $(C_6H_{11})_3Sn{\cdot}Sn(C_6H_{11})_3$, is prepared by the action of sodium on a solution of tin tri*cyclo*hexyl bromide in boiling xylene. It forms colourless, hexagonal platelets, stable towards light and air, decomp. slightly above 300°. Its molecular weight in concentrated solution corresponds with the formula $[Sn(C_6H_{11})_3]_2$, whereas the simpler molecular form appears to be present in more dilute solution.

Tin tricyclohexyl bromide, $(C_6H_{11})_3SnBr$, prepared from the crude product of the action of magnesium *cyclo*hexyl halide on stannic chloride (see above) by means of bromine in the presence of chloroform or carbon tetrachloride, crystallises in long, colourless prisms, m. p. 77°, decomp. about 280°. The corresponding *iodide* forms colourless, hexagonal plates, m. p. 65°, decomp. about 290°. The *fluoride* forms hexagonal prisms, decomp. about 305°. *Tin tricyclohexyl hydroxide*, colourless, hexagonal crystals, m. p. 220—222°, is prepared by shaking an ethereal solution of the bromide with an excess of potassium hydroxide solution (15%); when dehydrated, it yields the oxide, $(C_6H_{11})_3Sn{\cdot}O{\cdot}Sn(C_6H_{11})_3$. (Tin triphenyl hydroxide, long, hexagonal prisms, m. p. 119—120°, appears to be dehydrated similarly to the *oxide*, $Ph_3Sn{\cdot}O{\cdot}SnPh_3$; there is no evidence of the formation of different hydrates.) *Tin tricyclohexyl chloride*, obtained from the hydroxide and dilute hydrochloric acid, forms long, prismatic rodlets, m. p. 129—130°, decomp. about 286°; with ammonia it appears to yield the *compound*, $(C_6H_{11})_3SnCl,2NH_3$, m. p. 128° (decomp.).

Tin di*cyclo*hexyl dibromide, m. p. 58° (cf. Grüttner, *loc. cit.*), is hydrolysed to the corresponding *dihydroxide* (or *oxide*), a colourless, amorphous powder, m. p. 291° (decomp.) after darkening at 280° and softening at 287°. The corresponding *dichloride*, colourless, asbestos-like needles, m. p. 88—89°, decomp. about 220°, the *difluoride*, a colourless, microcrystalline powder, m. p. 278° after previous softening, and the di-iodide, a colourless, crystalline powder, m. p. 42° (Grüttner, *loc. cit.*, gives m. p. 145°), are described.

The following compounds are prepared by the action of a large excess of the requisite Grignard compound on tin tri*cyclo*hexyl bromide in ethereal solution: *Tin tricyclohexylmethyl*, $(C_6H_{11})_3SnMe$, a colourless, viscous liquid, b. p. 221°/15 mm., $d_4^{20\cdot7}$ (vac.) 1·1949, $n_D^{15\cdot7}$ 1·53979. *Tin tricyclohexylethyl*, a very viscous liquid, b. p. 227—228°/15 mm. (partial decomp.), $d_4^{15\cdot9}$ (vac.) 1·1875, $n_D^{15\cdot9}$ 1·53953. *Tin phenyltricyclohexyl*, colourless, microscopic crystals, m. p. 191—

192°; 0·65 g. dissolves in 100 g. of ethyl alcohol at 30·4°. *Tin* p-*tolyltricyclohexyl*, prismatic rodlets, m. p. 111°, which dissolves in ethyl alcohol to the extent of 0·70 g. in 100 g. at 30·4°. *Tin triphenylcyclohexyl*, colourless needles, m. p. 131—132°, is obtained from tin triphenyl chloride and magnesium *cyclo*hexyl bromide. H. W.

Peptisation of Gelatin by Mixed Liquids. E. W. J. Mardles (*Biochem. J.*, 1924, **18**, 215—230).—The peptisation of gelatin in mixtures of various solvents has been studied. The solubility of gelatin is greater in mixed liquids than the average value, and under some conditions the solvent power of water can be increased, or not appreciably diminished, by the addition of a non-solvent such as pyridine, glycerol, alcohol, etc. The theory of this phenomenon is discussed. S. S. Z.

Constitution of Proteins. N. Troensegaard and I. Schmidt (*Z. physiol. Chem.*, 1924, **133**, 116—125).—The authors bring forward evidence which they claim lends further support to the view that the protein molecule consists mostly of pyrrole derivatives containing oxygen. Acetylated gliadin, gelatin, and proteolic acid from gliadin were degraded by reduction into various fractions which showed properties characteristic of heterocyclic compounds. S. S. Z.

Proteins of Oats. H. Lüers and M. Siegert.—(See i, 597.)

Biochemistry.

Influence of Intravenous Injection of Protein on the Respiratory Exchange. E. Amstad (*Biochem. Z.*, 1924, **145**, 168—177).—In dogs, the average normal output of carbon dioxide per kilogram per minute is 9·5585 c.c. and the oxygen intake is 12·94 c.c. Intravenous injection of Ringer solution has a very slight effect in increasing the respiratory exchange; injection of foreign serum (horse) protein first lowers the exchange by 30% of its normal value, but later it rises above normal to the same extent, whilst injection of the serum-proteins of the dog itself produces the same effect as Ringer solution. J. P.

Physiology of Glands. LVIII. Possible Presence of Toxic Substances in the Sera of Thyroid- and Parathyroid-ectomised Animals in Relation to the Respiratory Exchange. L. Asher and K. Jino (*Biochem. Z.*, 1924, **145**, 105—115).—Intraperitoneal injection into rats of 1 to 2 c.c. of the sera of normal or thyroidectomised dogs increases the respiratory exchange, whilst sera from parathyroidectomised dogs with tetany lowers the respiratory exchange. It is concluded that whilst toxic substances are absent in the former case they may be present in the latter. J. P.

Physiology of Glands. LX. Respiratory Exchange of Normal and Splenectomised Rats. L. ASHER and Y. TAKAHASHI (*Biochem. Z.*, 1924, **145**, 130—153).—In general, removal of the spleen from rats diminishes the respiratory exchange, and increases the nitrogen excretion and the response to thyroid feeding as compared with the normal animals. The presence or absence of iron in the dietary has no influence on the respiratory exchange effect. Rats from which the spleen has been removed show a greater susceptibility to lack of oxygen than that shown by normal rats. The results are interpreted in favour of the view that the spleen and the thyroid are mutually antagonistic. J. P.

Physiology of Glands. LXI. Comparison of the Oxygen Consumption of Surviving Excised Mammalian Organs in the Normal Condition and after Thyroid Feeding. L. ASHER and A. ROHRER (*Biochem. Z.*, 1924, **145**, 154—167).—The isolated surviving liver, kidney, and muscle of mice which had been fed on thyroid consumed more oxygen than the same organs from normal animals. The respective figures found for 1 g. of each tissue per hour are: 639 and 784 c.mm., 818 and 941 c.mm., 791 and 985 c.mm. J. P.

Collection and Preservation of Blood Samples for Determination of Carbon Monoxide. R. R. SAYERS, H. R. O'BRIEN, G. W. JONES, and W. P. YANT (*U.S. Public Health Repts.*, 1923, 2005—2011. Reprint No. 863).—A modified Keidel tube method is described for the collection, transport, and storage of samples of 10—15 c.c. of blood in cases of carbon monoxide poisoning. A small vial, well-stoppered with a cork, will serve satisfactorily in emergency. For the inhibition of coagulation, sodium citrate (0·4 to 0·8 %) proved inefficient, sodium or potassium oxalate (0·2%) caused some change in the blood with a slight alteration in the carbon monoxide content, whilst sodium fluoride (0·3%) is recommended as being free from these objections. E. M. C.

Elimination of Carbon Monoxide from Blood by Treatment with Air, with Oxygen, and with a Mixture of Carbon Dioxide and Oxygen. R. R. SAYERS and W. P. YANT (*U.S. Public Health Repts.*, 1923, 2053—2074. Reprint No. 865).—Analyses of blood samples, made in carefully controlled experiments on three subjects, showed that the elimination of carbon monoxide depends on the percentage of oxygen in the air breathed and also on the rate and depth of respiration. Pure oxygen was about four times as efficient as ordinary air, whilst a mixture of oxygen containing 8 to 10% of carbon dioxide was about five to six times as efficient. E. M. C.

Seasonal Changes in the Gases and Sugar of the Blood, and the Nitrogen Distribution in the Blood and Urine of the Alligator. A. HOPPING (*Amer. J. Physiol.*, 1923, **66**, 145—163).—The oxygen capacity of the blood is highest (15·3) in March, and lowest (9·5) in May and June; the oxygen content of the venous

blood is lowest (1·8) in May and June and highest (11·0) in January and February. The carbon dioxide capacity and content are higher in spring than in summer or winter. Blood-sugar is high (0·095%) in spring and very low (0·0296%) in late autumn. The main nitrogenous constituent of the urine is ammonia; uric acid is present in the blood and urine in small amounts only.

CHEMICAL ABSTRACTS.

Influence of Oxygen Content on the Hydrogen-ion Concentration of the Blood. J. HOLLÓ and S. WEISS (*Biochem. Z.*, 1924, **145**, 10—13).—The p_H of human oxalated venous blood kept at a constant carbon dioxide content and oxygenated, is lowered by 0·03—0·06. J. P.

Experimental Tetany. III. Alkalosis and Acidosis. IV. Hydrogen-ion Concentration of the Blood. V. Alveolar Carbon Dioxide Tension. E. W. H. CRUICKSHANK (*Biochem. J.*, 1924, **18**, 47—62).—A change in the acid–base balance in parathyroid tetany, with the production of a condition of alkalosis, is observed in the primary or quiescent stage and is due to CO_2 deficit. With the development of acute tetany, this condition is changed into one of acidosis by the continuous loss of $BHCO_3$ and increase in H_2CO_3. The reaction of the blood as determined from CO_2 dissociation curves changes very slightly, the p_H increasing above normal for the animal by an average of 0·154 during the stage of alkalosis and falling with the introduction of the stage of acidosis. The alveolar CO_2 may fall as low as 1·975%, but with the continued loss of base there is a tendency for it to return towards the normal.

S. S. Z.

Chemical Pathology of Pyloric Occlusion in Relation to Tetany. Chloride, Carbon Dioxide, and Urea Concentrations in the Blood. H. A. MURRAY, jun. (*Arch. Surgery*, 1923, **7**, 166—196).—With stenosis of the pylorus, hydrogen chloride cannot pass into the intestines and be absorbed. It is expelled by vomiting or by gastric lavage. The result is a disturbance in the acid–base balance of the blood and tissues. The blood shows increased carbon dioxide and urea, and decreased chlorine. The most abnormal values found were: CO_2, 107% by vol.; Cl, 2·5 g. per l., and urea, 334 mg. per 100 c.c. of blood. There is a relation between these changes and the tetany which develops in severe cases. It is highly probable that nerve irritation is increased by a fall in the hydrogen-ion concentration of the blood or the sodium : calcium ratio. CHEMICAL ABSTRACTS.

Nature of the Red Blood-corpuscle. A. GOUGH (*Biochem. J.*, 1924, **18**, 202—214).—The red corpuscle is a fluid droplet the contents of which form a hydrophile colloidal system. The continuous phase (salts and water) constitutes one-third, the dispersed phase (hæmoglobin salts and water) two-thirds of this system. The surface film contains lipoids in a solid state, and all varieties of hæmolysis can be explained as due to disintegration of the envelope of the corpuscle. Crenation is due to protrusion through weak areas

in the envelope of the corpuscle. The characteristic shape of the corpuscle is due to tension of liquid surfaces tending to cause a spherical shape and to the repulsive forces between the dispersed particles of the corpuscular contents. S. S. Z.

Adsorption of Protein Degradation Products by Erythrocytes. N. Griasnov (*Biochem. Z.*, 1924, **145**, 63—65).—Contrary to the results of Sbarsky (A., 1923, i, 1252), biological methods of determining fixation reveal no adsorption of diphtheria toxin by erythrocytes *in vitro*. The disappearance of nitrite observed by Sbarsky and attributed by him to adsorption of protein degradation products is ascribed to oxidation by oxyhæmoglobin derived from hæmolysed erythrocytes. J. P.

Hæmoglobin and Methæmoglobin as Oxidative Catalysts. M. E. Robinson.—(See this vol., ii, 320.)

Lævulose in the Blood of the Human Fœtus. A. P. Orr (*Biochem. J.*, 1924, **18**, 171—172).—Human fœtal blood gives the Selivanov reaction, which shows the presence of lævulose. This sugar can also be demonstrated in the blood of the kid immediately after birth. S. S. Z.

Syphilis. V.—VIII. Arsenic Content of the Blood and Spinal Fluid after Neosalvarsan and Salvarsan Treatment. J. A. Fordyce, I. Rosen, and C. N. Myers (*Amer. J. Syphilis*, 1923, **7**, 444—559).—With neosalvarsan, arsenic was found, in quantities of 0·6—83·6 mg. per 100 g. of dried spinal fluid, at some time during the treatment in 22% of the cases; with salvarsan, after combined intravenous and intraspinal injections, arsenic was present in 88% of the fluids up to 73 mg., whereas after injection and drainage, arsenic was present up to 54·3 mg. in 83% of the specimens. The maximum amount of arsenic is present in the blood immediately after intravenous injection of silver salvarsan, but it quickly becomes localised outside of the circulating blood.

Chemical Abstracts.

Hydrogen-ion Concentration of Gastric Contents of Infants. F. L. Babbott, jun., J. A. Johnston, C. A. Haskins, and A. T. Shohl (*Amer. J. Diseases Children*, 1923, **26**, 475—485).—The normal range of the p_H of the gastric contents on the milk test meal at the end of an hour is p_H 3·2—5·0, with 76% of the readings between p_H 3·9 and p_H 4·6. The error of determining acidity of gastric contents from samples rather than from the entire contents is p_H 0·4. The acidity increases with increase in time. The previous type of feeding has no effect on the test meal. Acid production and hydrogen-ion concentration increase with increase of age. A fourfold increase of the concentration of the test meal decreases the hydrogen-ion concentration. A twofold increase of the amount of the test meal causes a stimulation of acid secretion, but a lessened acidity. The greater the gastric acidity, the more rapidly the stomach empties. Chemical Abstracts.

Metabolism of Carbohydrates. III. Absorption of Glucose, Fructose, and Galactose from the Small Intestine. J. A. HEWETT (*Biochem. J.*, 1924, **18**, 161—170).—Glucose, fructose, and galactose are absorbed from hypotonic solution from the small intestine, the rates of absorption decreasing in the order named. However, when the epithelial lining is destroyed, all three sugars are absorbed at the same rate. The results cannot be explained by osmosis or diffusion only. S. S. Z.

Production of Hypoglycæmia in Experimental Derangements of the Liver. M. BODANSKY (*Amer. J. Physiol.*, 1923, **66**, 375—379).—Hyperglycæmia is the initial effect of severe liver damage (severe chloroform or phosphorus poisoning). Subsequently this effect disappears and the blood-sugar falls to subnormal levels. Chloroform and phosphorus are general protoplasmic poisons, and death resulting from such acute poisoning is not due entirely to functional damage of the liver. CHEMICAL ABSTRACTS.

Physiology of Glands. LIX. Influence of Compensation on the Glycosuric Action of Subcutaneous Adrenaline Injections. L. ASHER and R. TSUKAMOTO (*Biochem. Z.*, 1924, **145**, 116—129).—The adrenaline glycosuria of thyroid-fed dogs which react strongly to the treatment, is, in some cases, more rapid but less intense than that of normal animals, but in others the glycosuria may be more intense than that of the normals. The results are explained on the basis of a double functioning of the thyroid hormone. Removal of blood or transfusion of a Ringer gelatin solution after bleeding produces a diminution in the response to adrenaline. J. P.

Preparation of Insulin. Alkaline Extraction of Pancreas. H. W. DUDLEY and W. W. STARLING (*Biochem. J.*, 1924, **18**, 147—150).—By the addition of sodium bicarbonate to the mixture of minced pancreas and alcohol the yield of insulin is increased nearly fivefold. An improved technique for the preparation of insulin hydrochloride through the picrate is also described, whereby at least 90% of the impurities in crude insulin can be removed. 0·2 Mg. of this preparation was found to be a "rabbit unit." S. S. Z.

Mode of Oxidation of Fatty Acids with Branched Chains. III. The Fate in the Body of α-Methylcinnamic Acid, β-Phenyl*iso*butyric Acid, and γ-Phenyl*iso*valeric Acid. H. D. KAY and H. S. RAPER (*Biochem. J.*, 1924, **18**, 153—160).—β-Phenyl*iso*butyric acid on oxidation in the body yields benzoic acid. The yield was 77% of the theoretical, assuming that β-oxidation alone had taken place. α-Methylcinnamic acid, which has been isolated as an intermediate product, also yields benzoic acid, but only to the extent of 33% of the amount expected if β-oxidation alone had taken place. No intermediate product could be isolated in this case. No difference was observed in the ease of oxidation in the body of the two isomorphous forms of α-methylcinnamic acid. γ-Phenyl*iso*valeric acid gives rise to phenylacetic acid on oxidation

in the body; the yield was not more than 50% of the amount expected if β-oxidation alone had taken place. S. S. Z.

Odd-carbon Fats in the Treatment of Diabetic Ketosis. M. KAHN (*Amer. J. Med. Sci.*, 1923, **166**, 826—833).—An odd-carbon fatty acid has been synthesised (the acid group of stearic acid is replaced by an organic radical and on oxidation the C_{17} acid is produced, which is united with glycerol) which is absorbed to about 90% and is catabolysed without the production of ketones. CHEMICAL ABSTRACTS.

Metabolism of Milch Cows suffering from Acetonæmia. B. SJOLLEMA and J. E. VAN DER ZANDE (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 666—668).—Analyses of blood, urine, and milk from cows suffering from acetonæmia show that waste of body fat takes place on a large scale, often about 1 kg. per diem. Lipæmia, glucosuria, and hyperglycæmia do not occur. The total quantity of acetone compounds in the urine may amount to about 120 g. per day. The cholesterol content of the blood is 50% to 100% higher than normal; sometimes it is even higher. The alkali reserve decreases. J. F. S.

Possibility of Influencing Decomposition of Albumin in the Body by Feeding Individual Amino-acids. R. W. SEUFFERT (*Z. Biol.*, 1924, **80**, 381—404).—Experiments on dogs receiving a diet containing insufficient protein show that whilst the feeding of individual amino-acids of the simplest type or an incomplete mixture of such acids never leads to an increase of body nitrogen or even to nitrogen equilibrium, an appreciable reduction in the daily loss of nitrogen from the body can be achieved by this means, which cannot be accounted for as merely the result of the additional calories brought to the diet by the amino-acids added. These results are checked and confirmed by a consideration of the daily loss of sulphur from the body with and without the addition of amino-acids to the diet. H. C. R.

Choline as a Precursor of Guanidine. Decrease in the Amount of Choline of the Hen's Egg during Incubation. J. S. SHARPE (*Biochem. J.*, 1924, **18**, 151—152).—There is a decrease in choline content of the hen's egg as incubation proceeds. It has been previously shown by Burns that the guanidine content increases during this period. The author suggests that choline is a possible source of guanidine in the animal body. S. S. Z.

Synthesis of Hippuric Acid in the Surviving Kidney of Various Animals and of Man. I. SNAPPER, A. GRÜNBAUM, and J. NEUBERG (*Biochem. Z.*, 1924, **145**, 40—46).—Perfusion of the isolated surviving kidney of the dog, sheep, pig, and man, with blood containing sodium benzoate and glycine, results in the synthesis of hippuric acid. J. P.

Sulphur Metabolism of the Dog. I. Synthesis of Ethereal Sulphate. T. S. HELE (*Biochem. J.*, 1924, **18**, 110—119).—Sodium sulphate, sodium hydrogen sulphite, and cystine are partly

excreted as ethereal sulphate by the dog when administered by the mouth together with guaiacol carbonate. The sodium sulphate is utilised as readily as cystine or as sodium hydrogen sulphite.
S. S. Z.

Calcium Fixation by Animal Tissues. R. E. Liesegang (*Biochem. Z.*, 1924, **145**, 96—97).—A criticism of the conclusions of Freudenberg and György (this vol., i, 242). J. P.

Mineral Metabolism of the Lactating and Dry Goat. C. H. Hunt, A. R. Winter, J. A. Schultz, and R. C. Miller (*Amer. J. Physiol.*, 1923, **66**, 349—362).—Balances were determined for sodium, potassium, calcium, magnesium, sulphur, chlorine, phosphorus, and nitrogen in dry and lactating goats on various diets, the mineral metabolism being found, in general, to be similar to that of the cow. The calcium and chlorine content of goat's milk is higher than of cow's milk. There is evidence that the calcium in green plants may be more highly dispersed, and hence better assimilated than that of dried feeds. Chemical Abstracts.

Nitrogen and Mineral Salt Metabolism in Avitaminosis. N. Hirabayashi (*Biochem. Z.*, 1924, **145**, 18—31).—In the avitaminosed dog, the body-weight may increase during the first few weeks, usually with increasing nitrogen retention, although towards the end of this period the nitrogen excretion may show an increase. With increasing duration of avitaminosis, the disturbed gastro-intestinal functioning is reflected in diminished body-weight and nitrogen excretion, and in the late stages a temporary increase in the nitrogen retention may set in. The nitrogen excretion is not an indication of the breakdown of nitrogen compounds in the body, since the residual nitrogen of the blood progressively increases in avitaminosis. The phosphorus, calcium, and magnesium balances in avitaminosis are parallel to the diminution in protein metabolism.
J. P.

Properties of certain South African Oils with Respect to Their Content of Vitamin-*A*. E. M. Delf (*Biochem. J.*, 1924, **18**, 93—100).—Sesamé, mafurreira, and castor oils are deficient in vitamin-*A*. Two samples of seal oil have been found to possess considerable growth-promoting properties. Samples of crude whale oil are active inversely to the temperatures used in the extraction. Sperm whale oil obtained from the head is the least active, and that obtained from the blubber is the most active in growth-promoting. When rats are deficient in vitamin-*A*, the addition of vitamin-*C* has a more beneficial effect than when the supply of vitamin-*A* in the diet is adequate. S. S. Z.

Relation of Vitamin-*A* Potency of the Liver Oil to the Sexual Condition and Age of the Cod. S. S. Zilva, J. C. Drummond, and M. Graham (*Biochem. J.*, 1924, **18**, 178—181).—The sexual condition and age of the cod do not influence the vitamin-*A* potency of the liver oil. S. S. Z.

Feeding Experiments in Connexion with Vitamin-*A* and -*B*. V. Orange Juice as a Source of Vitamin-*B*. VI. Ophthalmia in Rats affected with Avitaminosis. VII. The Vitamin Content of Cod-liver Oil and Malt Extract. A. D. STAMMERS (*Biochem. J.*, 1924, **18**, 9—15).—A daily dose of 10 c.c. of orange juice does not contain sufficient vitamin-*B* to promote growth in rats. The susceptibility of rats to keratomalacia varies directly with the amount of vitamin-*A* in the diet. Adult animals are less susceptible. "Cod-liver oil and malt extract" contains sufficient vitamin-*A* and -*B* to provide the necessary stimulus to growth. S. S. Z.

Vitamins. I. L. MARCHLEWSKI and Z. WIEVZCHOWSKI (*Bull. Soc. Chim. biol.*, 1924, **6**, 40—43).—Vitamin-*B* is better extracted from bran by dilute aqueous hydrochloric acid (0·1%) than by alcohol. From this solution, after neutralisation and filtration, addition of an ammoniacal solution of silver nitrate produces a greenish-brown precipitate containing the vitamin. This is dissolved out by hydrochloric acid, and after evaporating to dryness in a vacuum, and dissolving in water, a solution of great potency is obtained. From this solution, on the addition of picric acid, a yellowish-orange compound is precipitated, which may be recrystallised from acetone. A brownish-yellow solution of the vitamin, which has a characteristic odour, is obtained on decomposition of the picrate by dilute hydrochloric acid, and removal of the picric acid with ether. W. O. K.

The Reaction Proposed by Jendrassik as Characteristic of Vitamin-*B*, and its Relation with the Phenolic Grouping. M. N. BEZSSONOFF (*Bull. Soc. Chim. biol.*, 1924, **6**, 35—39).—The solution of ferric chloride and potassium ferricyanide, said by Jendrassik (A., 1923, ii, 892) to turn blue in presence of vitamin-*B*, is turned blue also by *o*- and *p*-phenols. Jendrassik is not justified in his conclusion that vitamin-*B* does not contain a phenolic group. W. O. K.

Antiscorbutic Fraction of Lemon Juice. I. S. S. ZILVA (*Biochem. J.*, 1924, **18**, 182—185).—A great part of the solids of decitrated lemon juice consists of invert-sugar. It is possible to ferment the sugar and thus reduce the solids without appreciably altering the antiscorbutic activity of the solution. The remaining solids seem to consist of substances mainly of a nitrogenous character. Some chemical characteristics of the active fraction are given. S. S. Z.

Conservation of the Potency of Concentrated Antiscorbutic Preparations. II. S. S. ZILVA (*Biochem. J.*, 1924, **18**, 186—187).—Concentrated decitrated lemon juice retains its antiscorbutic potency for five months if stored in acid solution in ampoules in a vacuum. S. S. Z.

Water- and Fat-soluble Growth Catalysts (*D*-Vitamins). H. VON EULER (*Ark. Kemi, Min., Geol.*, 1923, **8**, No. 31, 1—10).—From a top pressed yeast and a brewery yeast, by extraction with

water, dialysis through collodion membranes, concentration under a pressure of 1 mm., and precipitation by means of alcohol, the author has obtained preparations which effect very marked accelerations of fermentation either by living yeast or by washed dried yeast. With such preparations, however, there exists no parallelism between the influence on the growth of the yeast and that on the fermentation; moreover, no quantitative relationship is observable between the effects produced on the growth of yeast and of mice. In the light of these results the suggestion is made that the letter *D* be retained for growth factors but that D_r and D_m be used to denote the growth substance for rats or mice and for micro-organisms, respectively.

It is proposed further that the name vitamin be reserved exclusively for the following substances which act against definite vitamin-deficiency diseases: vitamin-*A* against rickets; vitamin-*B* against polyneuritis, and vitamin-*C* against scurvy. Substances which accelerate growth but may have nothing further in common with vitamins other than natural occurrence in low concentrations and certain properties relating to sorption, may be designated biocatalysts or growth-substances. In this way, the necessity of classifying Harden's co-zymase, hormones, etc., as vitamins is avoided.

As regards the effect on the growth of mice produced by cod-liver oil, at least one-fifth of the substances causing this effect is found to be transferable to aqueous-alcoholic or aqueous solution. The growth-substance obtained by extracting yeast with water is, however, removed to only a small extent from its concentrated aqueous solution when the latter is shaken with double its volume of a vitamin-free animal oil. T. H. P.

Separation of a Fat Pigment from Accompanying Fat. A. N. Currie (*Biochem. J.*, 1924, **18**, 231—234).—The fat is ground with lime and hydrolysed for 10 hours in an autoclave. The adipochrome goes mainly into the aqueous layer. The fatty acids are extracted with distilled water and the aqueous portions are combined and extracted with ether. The aqueous layer, which consists of pigment, salt, and glycerol, is acidified with 20% hydrogen chloride and extracted with ether. The adipochrome goes into the ether. S. S. Z.

Lipochrome of Adipose Tissue in Malignant Disease. A. N. Currie (*Biochem. J.*, 1924, **18**, 235—244).—The pigment is an unsaturated aliphatic hydrocarbon and is not related to carotene, xanthophyll, fucoxanthin, the anthocyanins, or the melanins. It is probably derived from the associated fats. The bearing of the adipochrome on the pathology of malignant disease is discussed. S. S. Z.

Hydrolysis of Hexose-diphosphoric Acid by Various Organs. Y. Takahashi (*Biochem. Z.*, 1924, **145**, 178—181).—Sodium hexose-diphosphate is hydrolysed *in vitro* by the kidneys, spleen, and muscle of the guinea pig, the activity of the organs diminishing in the order given (cf. also Tomita, A., 1922, i, 960). J. P.

Feeding Experiments in Connexion with Vitamin-*A* and -*B*. V. Orange Juice as a Source of Vitamin-*B*. VI. Ophthalmia in Rats affected with Avitaminosis. VII. The Vitamin Content of Cod-liver Oil and Malt Extract. A. D. STAMMERS (*Biochem. J.*, 1924, **18**, 9—15).—A daily dose of 10 c.c. of orange juice does not contain sufficient vitamin-*B* to promote growth in rats. The susceptibility of rats to keratomalacia varies directly with the amount of vitamin-*A* in the diet. Adult animals are less susceptible. "Cod-liver oil and malt extract" contains sufficient vitamin-*A* and -*B* to provide the necessary stimulus to growth. S. S. Z.

Vitamins. I. L. MARCHLEWSKI and Z. WIEVZCHOWSKI (*Bull. Soc. Chim. biol.*, 1924, **6**, 40—43).—Vitamin-*B* is better extracted from bran by dilute aqueous hydrochloric acid (0·1%) than by alcohol. From this solution, after neutralisation and filtration, addition of an ammoniacal solution of silver nitrate produces a greenish-brown precipitate containing the vitamin. This is dissolved out by hydrochloric acid, and after evaporating to dryness in a vacuum, and dissolving in water, a solution of great potency is obtained. From this solution, on the addition of picric acid, a yellowish-orange compound is precipitated, which may be recrystallised from acetone. A brownish-yellow solution of the vitamin, which has a characteristic odour, is obtained on decomposition of the picrate by dilute hydrochloric acid, and removal of the picric acid with ether. W. O. K.

The Reaction Proposed by Jendrassik as Characteristic of Vitamin-*B*, and its Relation with the Phenolic Grouping. M. N. BEZSSONOFF (*Bull. Soc. Chim. biol.*, 1924, **6**, 35—39).—The solution of ferric chloride and potassium ferricyanide, said by Jendrassik (A., 1923, ii, 892) to turn blue in presence of vitamin-*B*, is turned blue also by *o*- and *p*-phenols. Jendrassik is not justified in his conclusion that vitamin-*B* does not contain a phenolic group. W. O. K.

Antiscorbutic Fraction of Lemon Juice. I. S. S. ZILVA (*Biochem. J.*, 1924, **18**, 182—185).—A great part of the solids of decitrated lemon juice consists of invert-sugar. It is possible to ferment the sugar and thus reduce the solids without appreciably altering the antiscorbutic activity of the solution. The remaining solids seem to consist of substances mainly of a nitrogenous character. Some chemical characteristics of the active fraction are given. S. S. Z.

Conservation of the Potency of Concentrated Antiscorbutic Preparations. II. S. S. ZILVA (*Biochem. J.*, 1924, **18**, 186—187).—Concentrated decitrated lemon juice retains its antiscorbutic potency for five months if stored in acid solution in ampoules in a vacuum. S. S. Z.

Water- and Fat-soluble Growth Catalysts (*D*-Vitamins). H. VON EULER (*Ark. Kemi, Min., Geol.*, 1923, **8**, No. 31, 1—10).—From a top pressed yeast and a brewery yeast, by extraction with

water, dialysis through collodion membranes, concentration under a pressure of 1 mm., and precipitation by means of alcohol, the author has obtained preparations which effect very marked accelerations of fermentation either by living yeast or by washed dried yeast. With such preparations, however, there exists no parallelism between the influence on the growth of the yeast and that on the fermentation; moreover, no quantitative relationship is observable between the effects produced on the growth of yeast and of mice. In the light of these results the suggestion is made that the letter *D* be retained for growth factors but that D_r and D_m be used to denote the growth substance for rats or mice and for micro-organisms, respectively.

It is proposed further that the name vitamin be reserved exclusively for the following substances which act against definite vitamin-deficiency diseases: vitamin-*A* against rickets; vitamin-*B* against polyneuritis, and vitamin-*C* against scurvy. Substances which accelerate growth but may have nothing further in common with vitamins other than natural occurrence in low concentrations and certain properties relating to sorption, may be designated biocatalysts or growth-substances. In this way, the necessity of classifying Harden's co-zymase, hormones, etc., as vitamins is avoided.

As regards the effect on the growth of mice produced by cod-liver oil, at least one-fifth of the substances causing this effect is found to be transferable to aqueous-alcoholic or aqueous solution. The growth-substance obtained by extracting yeast with water is, however, removed to only a small extent from its concentrated aqueous solution when the latter is shaken with double its volume of a vitamin-free animal oil. T. H. P.

Separation of a Fat Pigment from Accompanying Fat. A. N. Currie (*Biochem. J.*, 1924, **18**, 231—234).—The fat is ground with lime and hydrolysed for 10 hours in an autoclave. The adipochrome goes mainly into the aqueous layer. The fatty acids are extracted with distilled water and the aqueous portions are combined and extracted with ether. The aqueous layer, which consists of pigment, salt, and glycerol, is acidified with 20% hydrogen chloride and extracted with ether. The adipochrome goes into the ether. S. S. Z.

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Determination, in Different Organs, of Polonium Injected into an Organism. (Mme.) J. S. Lattès and A. Lacassagne (*Compt. rend.*, 1924, **178**, 771—773; cf. this vol., i, 461).—The distribution, in the rabbit, of polonium, after the injection of the latter, whether intravenously, subcutaneously, or intraperitoneally, is approximately the same. The spleen and kidney are richest in polonium, the former retaining it longer than the latter. The liver, lungs, and especially the heart, rapidly lose their initial polonium. When polonium is injected into a pregnant mouse, the placenta is the organ richest in polonium, which is absent from the amniotic fluid and the fœtus. E. E. T.

Bio-radioactivity. P. Becquerel (*Compt. rend.*, 1924, **178**, 795—797).—Nodon's observation of bio-radioactivity (this vol., i, 347; cf. Berthelot, *ibid.*, i, 348) was made by Tommasina in 1904. Radioactive potassium is present in all animal and vegetable protoplasm, and until an improvement in technique enables its detection, the question of bio-radioactivity must remain open. E. E. T.

Liquid from *Tænia echinococcus*. O. Flössner (*Z. Biol.*, 1924, **80**, 255—260).—The presence of considerable amounts of sodium and chlorine and of lesser amounts of potassium, calcium, ammonium, and magnesium in the liquid from *Tænia echinococcus* was confirmed. Carbonic, sulphuric, and phosphoric acids were also present. The presence of glycogen, betaine, succinic acid, lactic acid, and purine bases was also established. The presence of betaine supports the theory of Kutscher and Ackermann that the metabolism of cold-blooded animals is similar to that of plants. The freedom of the liquid from albumin was confirmed. H. C. R.

Action of Rennet and of Heat on Milk. N. C. Wright (*Biochem. J.*, 1924, **18**, 245—251).—The action of rennet and heat (up to 120° for ½ hour) on caseinogen does not alter the racemisation curves, which suggests that no cleavage takes place in the molecule by the above treatments. Any changes brought about must therefore be of a physical nature. The coloration of autoclaved milk is due to the caramelisation of the lactose, a reaction which appears to be catalysed by the presence of a colloid substrate of calcium caseinogate. The colour of caseinogen precipitated from autoclaved milk is due to adsorption of this pigment. S. S. Z.

Cholesterol Content of Human Milk. F. W. Fox and J. A. Gardner (*Biochem. J.*, 1924, **18**, 127—135).—The total cholesterol of 1—12 days' milk is higher than the average of the later period of lactation in the ratios of 1 : 0·59. S. S. Z.

Acidity of Urine Measured by Physico-chemical Methods. C. O. Guillaumin (*Bull. Soc. Chim. biol.*, 1924, **6**, 14—25).—Emphasis is laid on the importance in urine analysis of the determination of p_H in addition to the usual titration methods. If the p_H is known, the fractions of the acids present that are ionised may be calculated. It is suggested that the ratio, v/V = c.c. of

N/10-hydrochloric acid required to change p_H from 8·0 to 4·0÷c.c. required to change p_H from 8 to 2·7, might be used to indicate the average degree of dissociation of the organic acids present in urine, but in practice this does not appear to give a trustworthy result. W. O. K.

Action of Sodium, Potassium, and Calcium Ions and of Uranyl Nitrate on the Spontaneous Rhythmic Movements of the Muscular Skin of the Earth-worm. P. C. HART (*Arch. Néerl. Physiol.*, 1924, **9**, 1—29).—The rhythmic movements which preparations of the muscular skin of the earth-worm execute when suspended in Ringer's solution have been studied. The effects of variations in the composition of the solution are, in general, similar to those obtained with isolated organs of other animals. The potassium chloride in the perfusion fluid may be replaced by uranyl nitrate; normal movements are obtained when 10 mg. of uranyl nitrate replace 100 mg. of potassium chloride (cf. *Annual Reports*, 1919, **16**, 148). E. S.

Action of some Physical and Chemical Agents on the Mobility of Ciliated Infusoria. E. and H. BIANCANI (*Compt. rend.*, 1924, **178**, 800—802).—Ciliated infusoria become permanently immobile under the influence of powerful ultra-violet radiation, a temporary immobility being produced by weak radiation. Salt solutions also induce immobility, isotonic solutions of different salts effecting the change at the same rate. Carbamide, ammonia, and iodine act similarly, the effect being proportional to the concentration. With all the agents mentioned, the dose–time curve is hyperbolic. E. E. T.

Action of Iodoethylurethane and Iodoethyl Allophanate. B. VON ISSEKUTZ and A. TUKATS (*Biochem. Z.*, 1914, **145**, 1—9).—Ethylurethane, iodoethylurethane, and acetyliodoethylurethane (CH_3·CO·NH·CO·OC_2H_4I) are increasingly toxic in the order given, whilst compared with the parent urethane, iodoethyl allophanate (NH_2·CO·NH·CO·OC_2H_4I) shows a diminished toxicity. The latter is absorbed in the intestinal tract to a greater extent than the iodine derivatives of the fatty acids, and is excreted in the urine approximately as rapidly and completely as potassium iodide. J. P.

Pharmacology of the Camphor Group. Comparison of an Isomeric Camphor with Japan Camphor. T. AMAKAWA (*Arch. Exp. Path. Pharm.*, 1924, **101**, 100—126).—The pharmacological action of 3-methyl-5-*iso*propyl-$\Delta^{2,3}$-*cyclo*hexenone (hexeton) is very similar qualitatively to that of camphor, but is several times stronger. W. O. K.

Bactericidal Action of the Tellurium Derivatives of Aliphatic β-Diketones. II. G. T. MORGAN, E. A. COOPER, and A. W. BURTT (*Biochem. J.*, 1924, **18**, 190—201).—These compounds are extremely germicidal for various strains of bacteria, the bactericidal power being determined by the symmetry of the parent β-diketone and by the presence of methyl and ethyl groups in para-

positions within the heterocyclic ring. Tellurium dipropionylmethane, fulfilling both these conditions of chemical structure, is therefore the most active of the series. The bactericidal power of these compounds increases considerably as the homologous series is ascended, until with the presence of an ethyl group and subsequent substitution of one methyl group, a limit is reached, and with further substitution of alkyl groups there is a diminution in efficacy. Position isomerism plays an important part in determining germicidal power. The tellurium compounds lose their strong bactericidal action in the presence of serum, but retain their inhibitory power. In urine, however, their germicidal power is retained. S. S. Z.

Comparative Germicidal Efficiency of Phenol, Mercuric Chloride, and Potassium Mercuri-iodide. J. C. CADORA [in part with R. W. LAMSON] (*J. Amer. Pharm. Assoc.*, 1923, **12**, 401—405).—The values without organic matter were 468·7 for mercuric chloride and 1100 for potassium mercuri-iodide. The minimum lethal dose for the three substances is 0·00035 g., 0·000012 g., and 0·000026 g., respectively. Compared with that of phenol as unity, the coagulating power of mercuric chloride is 55; no coagulating effect was observed with potassium mercuri-iodide. CHEMICAL ABSTRACTS.

Chemotherapeutic Researches in the Series 205 Baeyer. Carbamates of the Aminobenzoylaminonaphthalenesulphonic Acids. E. FOURNEAU, J. TRÉFOUËL, (MME.) J. TRÉFOUËL, and J. VALLÉE.—(See this vol., i, 382 and 504.)

Influence of certain Chemicals on the Rate of Reproduction of Yeast in Wort. N. A. CLARK (*J. Physical Chem.*, 1924, **28**, 221—231; cf. A., 1922, i, 501).—The rate of reproduction of yeast in wort at 25° follows a logarithmic law up to a certain limiting concentration, when the alcohol formed during fermentation begins to have an effect. The influence on this rate of phenol, methyl green, acetone, sodium bicarbonate, and hydrochloric and acetic acids has been studied. In general, the effect is to reduce the rate, which still, however, follows the logarithmic law. With increasing concentration of the poison there is also a resting period of increasing duration before reproduction begins. In every instance, a limiting concentration is reached above which no growth is observed, although it has been shown that this does not necessarily mean that the yeast is killed. When washed free from poison, it is still capable of reproduction. [Cf. *B.*, 1924, 395.] M. S. B.

Optimum Temperature of the Action of a Ferment or Lysin. I. BROWNLEE (*Biochem. J.*, 1924, **18**, 16—18).—The subject is treated mathematically. S. S. Z.

Nature, Constitution, and Mode of Action of Animal Tissue Enzymes. F. MAIGNON (*Compt. rend.*, 1924, **178**, 806—807; cf. this vol., i, 464).—Tissue and pancreatic enzymes, similar with regard to their content of metals, differ in their content of

acids (silicic, phosphoric, and arsenic in the former case and hydrochloric in the latter). The tissue enzymes may be written in the form, $(SiO_4)^{H.H.H.H.}$, etc., those of the pancreatic juice as $Cl^{H.}$. The paper contains other (theoretical) matter. E. E. T.

Inactivation of Invertase by Heavy Metals. K. Myrbäck (*Ark. Kemi, Min., Geol.*, 1923, **8**, No. 29, 1—37).—Experiments similar to those described by Euler and Svanberg (A., 1920, i, 689) have now been carried out with purer preparations of invertase. The extent to which the enzyme is inactivated by mercuric chloride varies greatly with the purity of the enzyme preparation, since the protein impurities are able to fix mercury and thus protect the enzyme; even with the most highly purified specimens of invertase, the first small additions of the mercury salt are without inactivating action. The purity of an invertase preparation is indicated by: (1) The absence, from the curve connecting relative activity with the proportion of mercuric chloride present, of the characteristic initial inflection that is shown when mercury-fixing impurities are present, (2) the constancy or gradual increase of the unimolecular reaction coefficient, and (3) the non-occurrence of auto-regeneration of the enzymic preparation.

Within the optimum zone, the inactivation by mercuric chloride is virtually independent of the hydrogen-ion concentration and, moreover, unlike what is the case with poisoning by silver, no acidity is capable of annulling the effect of the mercuric salt. Sucrose itself exerts a marked protective action. The mercury equivalent of invertase (per mol. of Hg) in the supposed compound Hg-invertase is calculated to be 3530, and the values $6{\cdot}6\times10^{-7}$ and $1{\cdot}0\times10^{-7}$ are found by two different methods for the dissociation constant of this compound.

With silver salts also, the amount needed to produce inactivation of invertase becomes very small when the enzyme is highly purified. Cysteine combines with very large proportions of silver, the acidity being without appreciable effect in this case. The poisoning action of copper or lead is similar to that of silver.

In view of the facts that the curve connecting the relative activity of the enzyme with the proportion of mercury present is a dissociation curve, that the acidity is without appreciable influence in the optimum zone, and that the poisoning is affected considerably by the concentration of the sucrose, it must be assumed that mercury forms with the enzyme a dissociating compound; in presence of sucrose, the invertase becomes distributed between the sugar and the mercury. With poisoning by silver, copper, or lead, other conditions must prevail, since the poisoning depends greatly on the acidity and is independent of the concentration of the substrate; in these cases, it is supposed that it is the enzyme-substrate compound which forms with the silver ion a very slightly dissociated salt.

Experiments on the influence of sodium acetate on the action of invertase yielded results similar to those obtained by Fales and Nelson (A., 1916, i, 174) with sodium chloride. T. H. P.

Inactivation of Invertase by Amines. K. MYRBÄCK (*Ark. Kemi, Min., Geol.*, 1923, 8, No. 32, 1—11).—The inactivation of invertase by *p*-toluidine as a function of the proportion of base present (cf. A., 1923, i, 496) is dependent only in slight degree on the hydrogen-ion concentration of the medium. Assuming that only the free enzyme, and not the enzyme–substrate compound, is able to fix the amine, values are derived for the dissociation constant of the enzyme–amine compound, which are virtually constant for different concentrations of the amine.

The degree of inactivation produced by aniline is not determined solely by the concentration of the base; the more acid solutions cause increased inactivation, which is due to an unknown factor. Ammonia inactivates invertase to as great an extent as do the aromatic amines. T. H. P.

Blood Enzymes. IV. Maltase of Dog's Serum: Influence on Activity of the Reaction of the Medium and of the State of Digestion. A. COMPTON (*Biochem. J.*, 1924, **18**, 173—177).—The maltase of the blood of the dog, like that of vegetable origin, requires an acid medium for its maximum activity (1·66 c.c. *N*/100 sulphuric acid to 55·5 c.c. of reaction mixture). The activity and the optimum temperature, *i.e.*, 55°, are the same whether the blood is collected during digestion or in the fasting state. S. S. Z.

Takalactase. C. NEUBERG and O. ROSENTHAL (*Biochem. Z.*, 1924, **145**, 185—188).—Takadiastase preparations contain an enzyme—*takalactase*—which hydrolyses lactose practically completely in 216 hours. Lactose osazone is similarly resolved into galactose and glucosazone. In the presence of yeast and takalactase, lactose gives rise to carbon dioxide. J. P.

Fructosediphosphatase in Human Organs. I. E. FORRAI (*Biochem. Z.*, 1924, **145**, 48—53).—Many dried human organs are capable of hydrolysing sodium fructosediphosphate, the percentage hydrolysis varying from 66% in the thyroids, to 19% in healthy muscle and 10% in blood-serum. A widespread distribution of fructosediphosphatase is inferred. J. P.

Differentiation of Human Phosphatases. E. FORRAI (*Biochem. Z.*, 1924, **145**, 54—56).—From comparative studies of the capacities of extracts of various human organs to hydrolyse glycero-, saccharo-, and fructosedi-phosphoric acids, it is concluded that the phosphatases concerned are different and specific enzymes. J. P.

Determination of the Activity of a Laccase. P. FLEURY (*Compt. rend.*, 1924, **178**, 814—816).—The activity of a laccase may be determined by aspirating air through the enzyme preparation in presence of guaiacol, the oxidation of which affords tetraguaiacoquinone. This substance is extracted with chloroform and determined colorimetrically. The lower the concentration of the laccase, the higher is its effectiveness, but, within certain limits, the ordinary linear relation holds between enzyme concentration and amount of substrate decomposed. Between these limits, the above method is accurate. E. E. T.

Mechanism of Oxidation in the Plant. II. Substances Capable of Behaving as Peroxydases. P. H. GALLAGHER (*Biochem. J.*, 1924, **18**, 29—38).—It is concluded that peroxydase activity is associated with aliphatic aldehydes, which do not act directly but after preliminary conversion by atmospheric oxygen into a substance of oxide nature. Peroxydase preparations prepared by alcoholic precipitation from the juices of vegetables such as the potato, the horse-radish, and the mangold contain a substance or substances of aldehydic nature. Oxides of some heavy metals induce oxidation of guaiaconic acid and of indophenol mixture by peroxide. The chemical nature of peroxydase action is discussed in the light of these results. S. S. Z.

Mechanism of Oxidation in the Plant. III. Peroxydase. Thermostability of the Peroxydase of the Mangold. P. H. GALLAGHER (*Biochem. J.*, 1924, **18**, 39—46).—Peroxydase of the mangold, inactivated by heat, becomes reactivated when the solution is allowed to remain some time in the cold. This reactivation has been studied quantitatively. The active and the inactivated solutions both contained iron and gave several reactions for aldehyde. Traces of iron added to aqueous solutions of aliphatic aldehydes give rise to an increase of peroxydase activity on standing in the cold. The zymogen of the peroxydase is probably an aldehyde which is activated by the catalytic action of iron after the inactivation by heat. S. S. Z.

Reaction of *Bacillus coli* applied to the Proteolytic Action of Serum (Abderhalden's "Ferments of Defence"). E. WOLLMAN, V. LABERNADIE, (MME.) E. WOLLMAN, and (MLLE.) J. OSTROWSKI (*Ann. Inst. Pasteur*, 1924, **38**, 115—151).—The production of indole from albumin by *Bacillus coli* only occurs after previous proteolysis of the albumin (Wollman, *Compt. rend. Soc. Biol.*, 1919, **82**, 1263). It is thus an indicator of such proteolysis, and may be used instead of the methods of dialysis or optical rotation in carrying out Abderhalden's reaction. The application of this method gave no evidence for the existence of the "ferments of defence" postulated by Abderhalden. W. O. K.

Extraction of Sap from Living Tissues by means of Compressed Air. H. H. DIXON and N. G. BALL (*Sci. Proc. Royal Dubl. Soc.*, 1924, **17**, 263—266).—Liquid was forced out of the wood and leaves of branches by enclosing them in a strong cylinder, in such a way that their cut ends protruded, and increasing the pressure in the cylinder to about 20 atmospheres. This liquid was almost completely free from sugars, except when the leaves had been exposed to toluene vapour. The transport of carbohydrates from the leaves to the stem through the wood involves, in addition to a backward flow through the tracheæ, an increased permeability of the leaf cells. E. M. C.

Physiological Studies on Apples in Storage. J. R. MAGNESS and H. C. DIEHL (*J. Agric. Res.*, 1924, **27**, 1—38).—The changes in apples after picking are, in the main, a continuation of those

occurring during ripening on the tree. The softening of stored apples is accelerated by increased temperature. The decrease in acidity during storage was practically the same for all varieties of apples, and was independent of the original acidity. Coating the surface of apples with oil or similar material, by reducing the gaseous exchange, retards ripening. So long as anaërobic respiration does not occur, the flavour of the fruit is not detrimentally affected. The higher the temperature of storage, the smaller is the thickness of the coating which will bring about anaërobic respiration and bad flavour. The retardation of ripening appears to be due both to the reduced amount of oxygen and the increased amount of carbon dioxide in the intracellular spaces. Storage of apples in an atmosphere containing up to 10% of carbon dioxide delayed softening, with no apparent loss of quality, but greater proportions caused a bad flavour. A. G. P.

Essential Oil of Manuka (*Leptospermum Scoparium*). R. GARDNER (*J. Soc. Chem. Ind.*, 1924, **43**, 34—35T).—The leaves of the New Zealand wild shrub known as "manuka" yield about 0·45% of greenish-yellow essential oil, d^{15} 0·921, n_D 1·50, b. p. 160—270°/760 mm. The oil consists approximately of phenols (leptospermol), 2·8%; terpenes, 2·8%; cinnamic esters (calculated as ethyl cinnamate), 4·8%; other esters (calculated as $CH_3 \cdot CO_2 \cdot C_{10}H_{15}$), 12·9%; semi-solid, non-volatile substances, 7·7%; sesquiterpene, 69·0%. W. P. S.

Protein and Vitamin-*A* Content of the English Walnut. H. L. MIGNON (*Amer. J. Physiol.*, 1923, **66**, 215).—Tannins present in the skins of English walnuts interfere with the extraction of the walnut globulin and constitute a growth-limiting factor in the diets of rats and mice. Vitamin-*A* is present in extremely small amounts. The distribution of nitrogen as amino-acids in walnut globulin, as determined by Van Slyke's method, is: cystine, 0·86; amide, 9·99; humin, 1·84; arginine, 39·13; histidine, 5·74; lysine, 10·61; monoamino-, 30·26; non-amino-, 0·88%.

CHEMICAL ABSTRACTS.

Relation between the Chemical Structure of Bile Acids and their Phytopharmacological and Zoöpharmacological Reactions. D. I. MACHT and O. R. HYNDMAN (*J. Pharm. Exp. Ther.*, 1924, **22**, 483—490).—The inhibition of the growth of seedlings by taurocholic and glycocholic acids appears to be due to the cholic acid in the molecules, since glycine and taurine have little or no action on the growth of seedlings (*Lupinus albus* or *Vicia faba*) or on the reactions of rats in a circular maze, whilst cholic (and also choloidinic) acid is very active. W. O. K.

Saponin of *Panax repens*, Maxim. I. Y. MURAYAMA and T. ITAGAKI (*J. Pharm. Soc. Japan*, 1923, No. 501, 783—789; cf. Inoue, *ibid.*, 1902, No. 242, 356).—After treatment with ether, crushed *Panax repens*, Maxim, was extracted with hot alcohol; from the extract a saponin (5%) was isolated as a white, amorphous powder (m. p. 180—190°), which has a bitter taste.

When shaken with water, it dissolves slightly with foaming; it gives a clear solution on the addition of sodium carbonate. It behaves as an acid, thus supporting the hypothesis of Asahina and Momotani (*ibid.*, 1914, No. 384, 117). It contains 0·33% of ash. When hydrolysed with 3% hydrochloric acid it gave dextrose and a sapogenin (15%). The latter was obtained as white, lustrous needles (m. p. 303—304°). The sapogenin gives the same colour reactions as the saponin, but has no taste. It gives two diacetyl derivatives: one, plates (m. p. 207—210°), and the other, needles (m. p. 257—260°). K. K.

Isolation and Identification of Rutin from the Flowers of Elder (*Sambucus Canadensis*, L.). C. E. Sando and J. U. Lloyd (*J. Biol. Chem.*, 1924, **58**, 737—745).—The yellow pigment "eldrin" from the flowers of the elder (Lloyd, *Eclectic Med. J.*, 1920, **80**, 591) is shown to be identical with rutin from *Eschscholtzia* (Sando and Bartlett, A., 1920, i, 446) in its appearance, composition, products of acid hydrolysis (quercetin, dextrose, and rhamnose), and in its absorption spectrum. The yield of quercetin on hydrolysis is slightly higher than that calculated, owing to the presence of an impurity. G. M. B.

Proteins of Oats. H. Lüers and M. Siegert (*Biochem. Z.*, 1924, **144**, 467—476).—Various protein fractions prepared from oats by Osborne's methods, and belonging to the alcohol-, salt-, and alkali-soluble groups, were examined for their products of hydrolysis. The results are given in tabular form. The differences between the alcohol-soluble proteins of oats and those of the other cereals lie chiefly in the higher cystine and in the medium histidine content. The globulins of oats contain less arginine and decidedly more non-amino nitrogen than the globulins of other cereals. Avenaline, the protein characteristic of oats, is rich in arginine and histidine. Although there are many points of similarity between the nitrogen distribution of the proteins of oats and of other cereals, there is not a complete agreement. The proteins of oats are therefore to be regarded as a distinct group. S. S. Z.

Influence of Phylogeny on the Constitution of the Alkaloids. J. Gadamer (*Pharm. Monatsh.*, 1923, **4**, 157—160; from *Chem. Zentr.*, 1924, i, 56).—Certain families of plants yield characteristic alkaloids. From this fact it is possible to draw conclusions as to the constitution of alkaloids from different species of the same family. G. W. R.

Basic Substances from the Juice of the Alfalfa Plant [Lucerne]. C. S. Leavenworth, A. J. Wakeman, and T. B. Osborne (*J. Biol. Chem.*, 1923, **58**, 209—214).—The filtrate obtained from the press-juice after precipitation by addition of 53% by weight of alcohol (A., 1922, i, 1104) has been hydrolysed by boiling for 12 hours with 25% sulphuric acid and the product examined for basic substances according to Kossel's method. The following substances were isolated: arginine, stachydrin (cf. Steenbock, A., 1917, i, 439), lysine, and a *compound* which was apparently a purine

derivative. The latter was obtained from the mercuric sulphate fraction and gave a *picrate*, silky needles, m. p. 298°, and a *hydrochloride* (?), long plates, m. p. about 252°, which contained 31·8% of nitrogen. It is not known whether these bases are present in the press-juice in the free state or whether they are liberated during hydrolysis. Van Slyke's method for analysing the hydrolytic products of proteins is not applicable to the water-soluble constituents of forage plants. E. S.

Extraction of Nitrogenous Constituents from Plant Cells. W. E. TOTTINGHAM, E. R. SCHULZ, and S. LEPKOVSKY (*J. Amer. Chem. Soc.*, 1924, **46**, 203—208).—The investigation deals with the efficiency of various methods of desiccation and extraction as related to the proportions of total soluble nitrogenous compounds and soluble proteins in leaves of the barberry and sugar beet. The influence of freezing and drying on the distribution of nitrogen in plant cells is discussed. The results obtained indicate the desirability of extracting with water as general usage in fractionating the nitrogenous constituents of plant cells; water extracts the greater part of the proteins exposed by crushing the cells of fresh tissue. Chibnall's method of extraction does not sharply separate non-protein from protein nitrogen. F. A. M.

Presence of Vernine (Guanosine) in the Green Leaves and Berries of the Coffee Tree (*Coffea Arabica*, L.) and its Relation to the Origin of Caffeine in this Plant. T. DE A. CAMARGO (*J. Biol. Chem.*, 1924, **58**, 831—834).—A pentoside containing guanine, found in the green leaves and berries of this species, is probably the guanosine previously found in several plants (Schultze, A., 1886, 157, 736) and in nucleic acid (Levene and Jacobs, A., 1909, i, 620). This substance is probably the origin of caffeine in the leaves and berries of the coffee tree. It is transformed by enzymes to guanine, then to xanthine, and finally to caffeine. G. M. B.

Method for Sterile Cultures of the Higher Plants. E. BOBKO (*Z. Pflanz. Düng.*, 1924, **A**, **3**, 41—44).—The apparatus consists of a wide-necked vessel, to hold the nutrient solution, inside the wide neck of which is a piece of net stretched on a frame. The whole is covered with a dome-shaped cap, having cottonwool-plugged tubulures through which seed and sand may be introduced. The lower vessel has a side tube through which an air current or renewed nutrient solution may be passed. The vessel and solution are first sterilised; the seeds are separately sterilised and then introduced on to the gauze and covered with sterile sand. The cover is then removed. A. G. P.

Comparison of the Soil Solution by the Displacement Method and the Water Extract of Alkali Soils. P. L. HIBBARD (*Soil Sci.*, 1923, **16**, 465—471).—When the composition of 1 : 5 water extracts of nine alkali soils was used as a basis for the calculation of the composition of the soil solution, results were obtained which were at variance with those given by an analysis of the

solution obtained from the same soil by the displacement method (A., 1921, i, 214). Only in the case of chlorides, nitrates, and sodium were the results given by the two methods in approximate agreement. Calcium and magnesium may be either under- or over-estimated by the water extract method. All the other ions were over-estimated to varying degrees. Analysis of 1 : 5 water extracts of soils is thus liable to give a distorted and, usually, an unfavourable impression as to the composition of the soil solution and the suitability of the soil for plant growth. H. J. P.

Replacement of Soil Potassium. S. C. VANDECAVEYE (*Soil Sci.*, 1924, **17**, 91—96).—Organic manures (clover hay and dung) increased the amount of replaceable potassium in soil (as determined by neutral salt extraction) proportionally to the amounts added. Evidence is given that this liberation of replaceable potassium is largely a chemical phenomenon, and is not the result of biological activities or the production of carbon dioxide in the soil. A. G. P.

Reciprocal Repression Exerted by Calcic and Magnesic Additions upon the Solubility of Native Materials in Surface Soil. W. H. MACINTIRE, W. M. SHAW, and J. B. YOUNG (*Soil Sci.*, 1923, **16**, 449—464).—Lysimeter experiments are recorded in which magnesium and calcium compounds were added to the soil in varying quantities and with the supplementary use of sulphur compounds. In all cases, the addition of lime increased the calcium content of the drainage water and depressed that of magnesium. The reverse occurred when magnesia was substituted for lime. Ferrous sulphate, pyrites, and sulphur each increased the drainage losses of calcium and magnesium; but if used in conjunction with lime, the calcium losses were further increased and those of magnesium lessened. Similarly, magnesia, coupled with either of the sulphur compounds, brought about increased leaching of magnesium, and a depression of the loss of calcium normally occasioned by the sulphur compounds alone. Lime and magnesia in soil slowly revert to an insoluble and unavailable condition. Excessive liming may so depress the solubility of magnesium salts, as to cause a chlorotic condition in plants due to deficiency of magnesium. A. G. P.

Effect of Soil Suspensions on the Solubility of the Sulphate Radical in the System $Ca(OH)_2$–$CaSO_4$–H_2O. W. H. MACINTIRE and W. M. SHAW (*Soil Sci.*, 1924, **17**, 65—89).—In small amounts lime increased the amount of dissolved sulphate in a ferrous sulphate–soil–water suspension. Larger amounts of lime, however, almost eliminated dissolved sulphates from the suspensions, even when a period was allowed, before adding lime, for the reaction between soil and ferrous sulphate to proceed. If the excess of lime were removed from the soil suspension by the addition of sodium carbonate or by carbon dioxide the depressive effect on the solubility of sulphates disappeared. Here also the same effects were observed when the addition of sodium carbonate

was delayed. The addition of soil to solutions of calcium sulphate caused the removal of considerable amounts of sulphate from solution. Similar experiments are recorded in which calcium carbonate, magnesium oxide, and carbonate were used in conjunction with ferrous sulphate (cf. *Soil Sci.*, 1923, **16**, 159). Soil structure played an important part in sulphate adsorption. Ignited soil contained more soluble sulphate than the fresh sample, but also adsorbed more sulphate from added solutions, and the effects of lime were accentuated. Greater quantities of sulphate were removed by extracting soil with large amounts of water than by rainwater leaching in lysimeters. A. G. P.

Factors affecting the Growth of Crops on Acid Soils. S. D. Conner (*Ind. Eng. Chem.*, 1924, **16**, 173—175).—The capacity of a soil to neutralise calcium hydroxide, carbonate, or acetate is a measure of the total acidity, both organic and inorganic. Methods depending on the action of a salt of a strong acid and a strong base, such as potassium nitrate, give a measure of the inorganic acid silicates, but not to any great extent of the organic acids. The expression (inorganic acidity)^2/(organic acidity) gives a better indication of the lime needs of both organic and inorganic soils than that given by any single method of determining acidity. The toxicity of soil acidity may be due to both aluminium ions and hydrogen ions. Some crops, such as maize and radishes, are more sensitive to aluminium ions than to hydrogen ions, whilst others, such as red clover and beets, are more sensitive to hydrogen ions than to aluminium ions. Both phosphates and lime are needed to correct the toxicity of aluminium and hydrogen ions in most acid soils. H. C. R.

Behaviour of Lime in the Soil. O. Lemmermann and L. Fresenius (*Z. Pflanz. Düng.*, 1924, **A**, **3**, 1—20).—The relationship between the action of various calcium compounds on soils was determined by shaking together soil and various salt solutions. Calcium, supplied to soil as chloride or bicarbonate, was "fixed" largely by base exchange in accordance with the usually accepted views. If slaked lime was used, the calcium was held by adsorption. Carbon dioxide can partly, but not wholly, remove calcium from this adsorbed condition. The addition of calcium hydroxide to soils accelerated the decomposition of organic matter. This occurred even when the amount of calcium hydroxide added was so adjusted that the whole of it would be adsorbed by the soil colloids. The addition of small amounts of lime to soil suspensions caused increased dispersion of the clay, larger amounts producing the normal flocculation. The permeability to water of soil to which successively increasing amounts of lime were added decreased with the smaller additions, and increased as the proportion of lime was further increased. A. G. P.

Determination of Acidity of Soils. R. M. Barnette and others.—(See this vol., ii, 347.)